

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
12 May 2005 (12.05.2005)

PCT

(10) International Publication Number  
**WO 2005/042176 A1**

(51) International Patent Classification<sup>7</sup>: **B05D 3/02**

(21) International Application Number:  
PCT/US2004/036116

(22) International Filing Date: 28 October 2004 (28.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/696,057 29 October 2003 (29.10.2003) US

(71) Applicant (for all designated States except US): **E.I. DUPONT DE NEMOURS AND COMPANY** [US/US];  
1007 MARKET STREET, WILMINGTON, Delaware  
19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **UCKERT, Frank, P.**  
[DE/US]; 545 Willow Lane, Buellton, California 93427  
(US).

(74) Agent: **CAPRIA, Mary, Ann**; E. I. DU PONT DE  
NEMOURS AND COMPANY, LEGAL PATENT  
RECORDS CENTER, 4417 Lancaster Pike, Wilmington,  
Delaware 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LIGHT-EMITTING COPOLYMERS AND ELECTRONIC DEVICES USING SUCH COPOLYMERS

(57) Abstract: The invention provides novel pentaphenylene copolymers which are useful in electronic devices.

WO 2005/042176 A1

TITLELIGHT-EMITTING COPOLYMERS AND ELECTRONIC DEVICES  
USING SUCH COPOLYMERSTHE INVENTION

5           The invention relates generally to pentaphenylene copolymers, and their use in electronic devices.

BACKGROUND INFORMATION

          Organic electronic devices are present in many different kinds of electronic equipment. In such devices, an active layer is sandwiched  
10   between two electrical contact layers. At least one of the electrical contact layers is light-transmitting so that light can pass through the electrical contact layer. One type of electronic device is an organic light emitting diode (OLED), which holds promise for display applications due to its high power conversion efficiency and low processing costs. Such displays are  
15   especially promising for battery-powered, portable electronic devices, including cell-phones, personal digital assistants, handheld personal computers, and DVD players. These applications call for displays with high information content, full color, and fast video rate response time in addition to low power consumption.

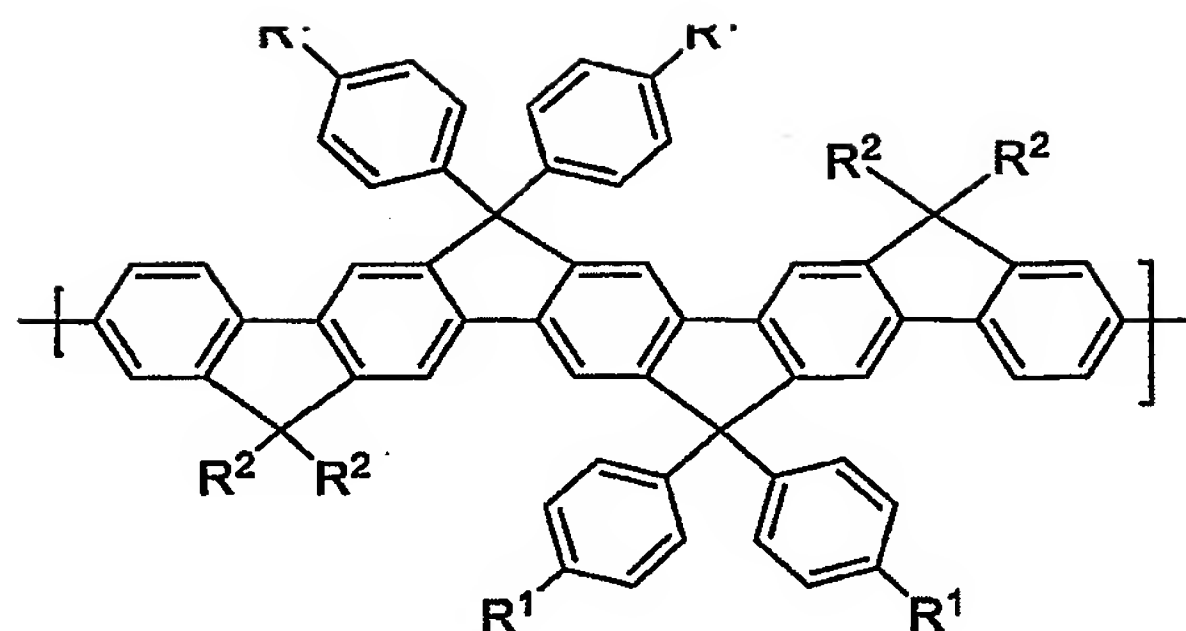
20           OLED's typically contain electroluminescent (EL) layers arranged between an anode and a cathode. Types of electroluminescent materials which have been used in OLED's include fluorescent dyes, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. Several classes of luminescent polymers have also been  
25   disclosed. These include, for example, poly(1,4-phenylene vinylene) and derivatives; polythiophenes, especially, poly(3-alkylthiophenes); and poly(p-phenylenes). Alkyl and dialkyl derivatives of polyfluorene have also been disclosed.

          There is a continuing need for active compounds having the necessary  
30   efficiency and color. In particular, blue-emitting polymers are desirable.

SUMMARY OF THE INVENTION

          The invention provides a copolymer comprising a first monomeric unit having Formula I below:

35



(I)

wherein:

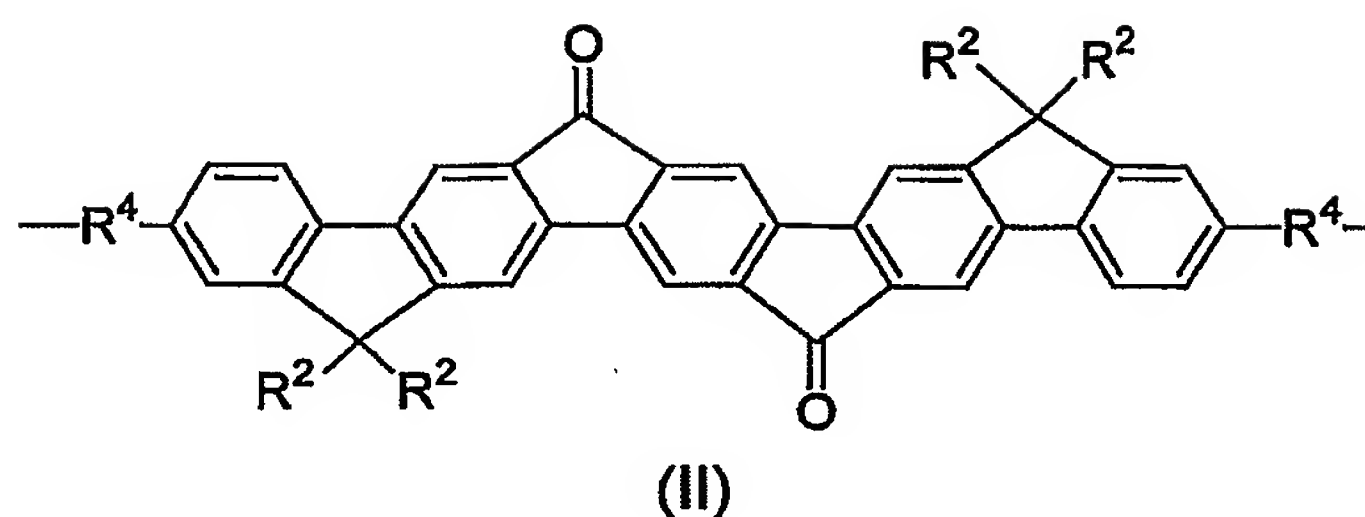
5  $R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

15  $R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

25  $R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

and at least one second monomeric unit comprising an aromatic group.

In one embodiment, the invention relates to a copolymer comprising the first monomeric unit and a second monomeric unit having Formula II  
30 below:



5 wherein:

$R^2$  is as defined above, and

$R^4$  is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

10 In one embodiment, the invention relates to an electronic device having an active layer comprising at least one of the above copolymers.

As used herein, the term "aromatic group" is intended to mean an organic group comprising at least one unsaturated cyclic group having delocalized pi electrons. The term is intended to encompass both  
 15 aromatic hydrocarbon groups having only carbon and hydrogen atoms, and heteroaromatic groups wherein one or more of the carbon atoms within the cyclic group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "alkyl" refers to a monovalent straight or branched chain hydrocarbon group. The term "alkylene" refers to an alkyl  
 20 group having two points of attachment.

As used herein, "alkoxy" refers to the moiety -O-alkyl-, wherein alkyl is as defined above.

As used herein, "oxyalkyl" refers to alkyl moieties in which at least  
 25 one -CH<sub>2</sub>- unit of the alkyl moiety has been replaced by an oxygen atom.

As used herein, "alkenyl" refers to straight or branched chain hydrocarbyl groups having one or more carbon-carbon double bonds.

As used herein, "oxyalkenyl" refers to alkenyl moieties in which at least one -CH<sub>2</sub>- unit of the alkenyl moiety has been replaced by an oxygen  
 30 atom.

As used herein, "alkynyl" refers to straight or branched chain hydrocarbyl groups having one or more carbon-carbon triple bonds.

As used herein, "oxyalkynyl" refers to alkynyl moieties in which at least one -CH<sub>2</sub>- unit of the alkenyl moiety has been replaced by an oxygen atom.

As used herein, "fluorinated" means that at least one hydrogen atom of the moiety has been replaced with a fluorine atom.

As used herein, the terms "heteroalkyl", "heteroalkenyl", and "heteroalkynyl" are intended to mean an alkyl group, an alkenyl group, and an alkynyl group, respectively, wherein one or more of the carbon atoms within the group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "aryl" is intended to mean a group derived from an aromatic hydrocarbon which may be unsubstituted or substituted. The term "arylene" refers to an aryl group having two points of attachment. The term "heteroaryl" is intended to mean an aryl group, wherein one or more of the carbon atoms within the aryl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "active material" is intended to mean a material which is electrically active or photoactive. Electrically active materials include conductive and semiconductive materials. The term "photoactive" refers to any material that exhibits electroluminescence, photoluminescence, and/or photosensitivity.

As used herein, the term "blue," is intended to mean any color that appears bluish to the naked human eye, including light of wavelengths ranging from 400 nm to 540 nm.

As used herein, the term "emission maximum" is intended to mean the wavelength, in nanometers, at which the maximum intensity of electroluminescence is obtained. Electroluminescence is generally measured in a diode structure, in which the material to be tested is sandwiched between two electrical contact layers and a voltage is applied. The light intensity and wavelength can be measured, for example, by a photodiode and a spectrograph, respectively.

As used herein, the term "monomeric unit" is intended to mean a repeating unit within a polymeric structure.

As used herein, the term "degree of polymerization" is intended to mean the total number of monomeric units in a polymer.

The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1-18 (CRC Handbook of Chemistry and Physics, 81<sup>st</sup> Edition, 2000).



As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of the "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In the formulae, all letters not otherwise defined, are used to designate conventional atomic symbols. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated by way of example and not limitation in the accompanying figures.

FIG. 1 includes an illustration of a cross-sectional view of an electronic device that includes a polymer in accordance with an embodiment of the present invention.

Skilled artisans appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures

may be exaggerated relative to other elements to help to improve understanding of embodiments of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The copolymer of the invention has a first monomeric unit having  
5 Formula I above which comprises a planar ladder-type pentaphenylene unit. This structure is intermediate between the monomeric units in fully ladder-type poly(p-phenylene) polymers ("LPPP") (reviewed by Scherf, *J. Mater. Chem.*, 1999, 9, 1853) and fluorene monomeric units (recent reviews are Neher, *Macromol. Rapid Commun.*, 2001, 22, 1365 and  
10 Scherf and List, *Adv. Mater.*, 2002, 14, 477).

In the copolymers of the invention the rigidity of the first monomeric unit structure produces a small Stokes shift and high fluorescence efficiency. The aryl substituents improve the stability of the polymer against oxidation as previously shown in polyfluorenes (Müllen et al,  
15 *JACS*, 2001, 123, 946; *Adv. Mater.*, 2002, 13, 809), while the avoidance of polymer analogous reaction steps avoids defects due to incomplete ring closure as is possible in LPPP.

The copolymers of the invention may exhibit blue electroluminescence. In one embodiment, the copolymer has an emission  
20 maximum less than 450 nm.

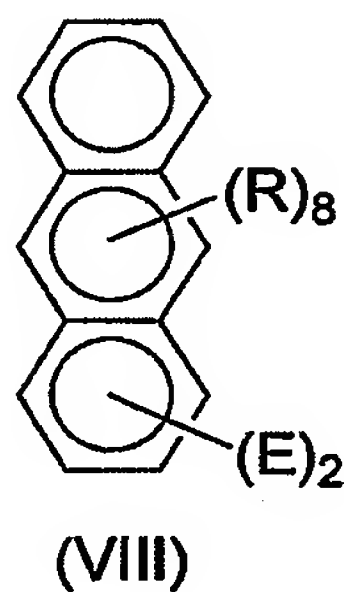
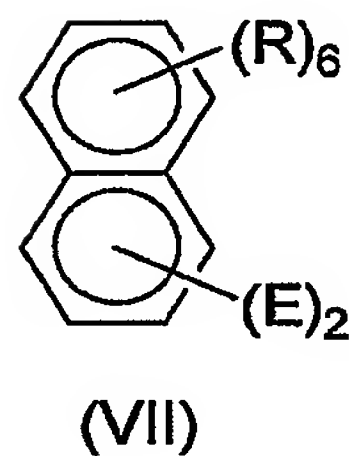
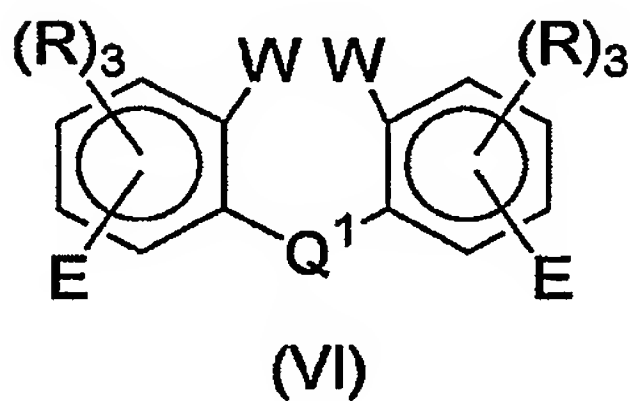
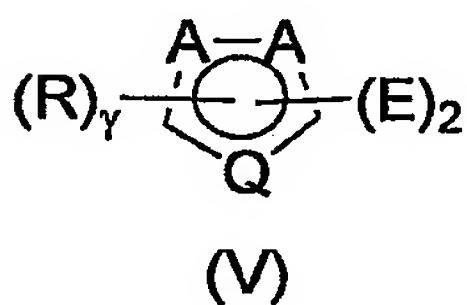
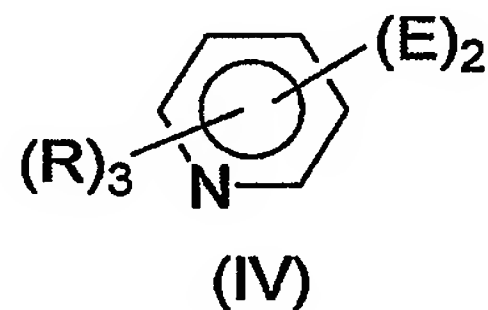
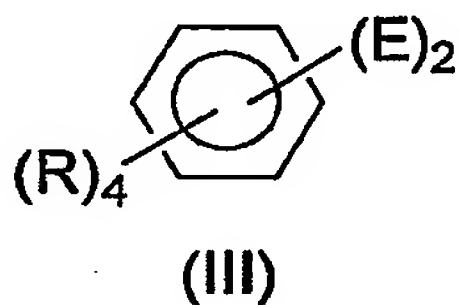
In one embodiment of Formula I, R<sup>1</sup> is selected from C<sub>1-20</sub> alkyls. In one embodiment, R<sup>1</sup> is selected from C<sub>1-10</sub> alkyls. In one embodiment all R<sup>1</sup> groups are the same. In one embodiment R<sup>2</sup> is selected from C<sub>1-20</sub> alkyls. In one embodiment R<sup>2</sup> is selected from C<sub>1-10</sub> alkyls. In one  
25 embodiment all R<sup>2</sup> groups are the same.

In the copolymers of the invention, there is at least one second monomeric unit comprising an aromatic group. Such monomeric units can be derived from mono- and polycyclic aromatic hydrocarbons and heteroaromatics. Examples of suitable aromatic groups include, but are  
30 not limited to, fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and the like, including mono- and poly-hetero analogs, and combinations thereof. The aromatic group can be substituted at one or more positions.

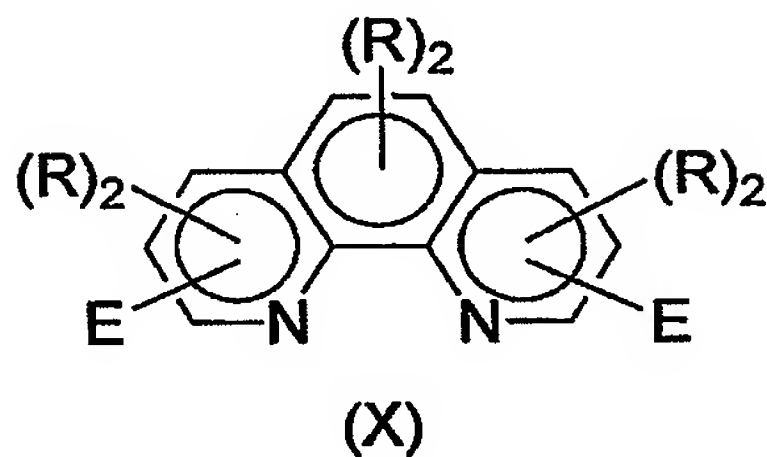
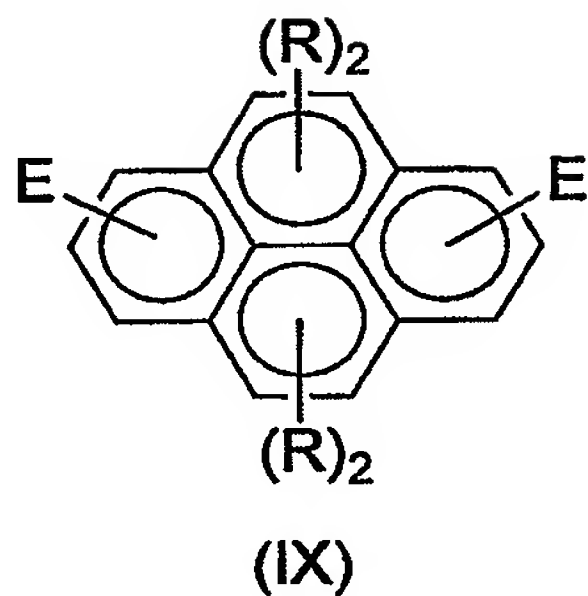
In one embodiment of the invention, the second monomeric unit  
35 comprises Formula II. This monomeric unit has an electron accepting property. In one embodiment of Formula II, R<sup>4</sup> is selected from a single bond and a phenylene. In one embodiment all R<sup>4</sup> groups are the same. In one embodiment R<sup>2</sup> is selected from C<sub>1-20</sub> alkyls. In one embodiment R<sup>2</sup>

is selected from C<sub>1-10</sub> alkyls. In one embodiment all R<sup>2</sup> groups are the same.

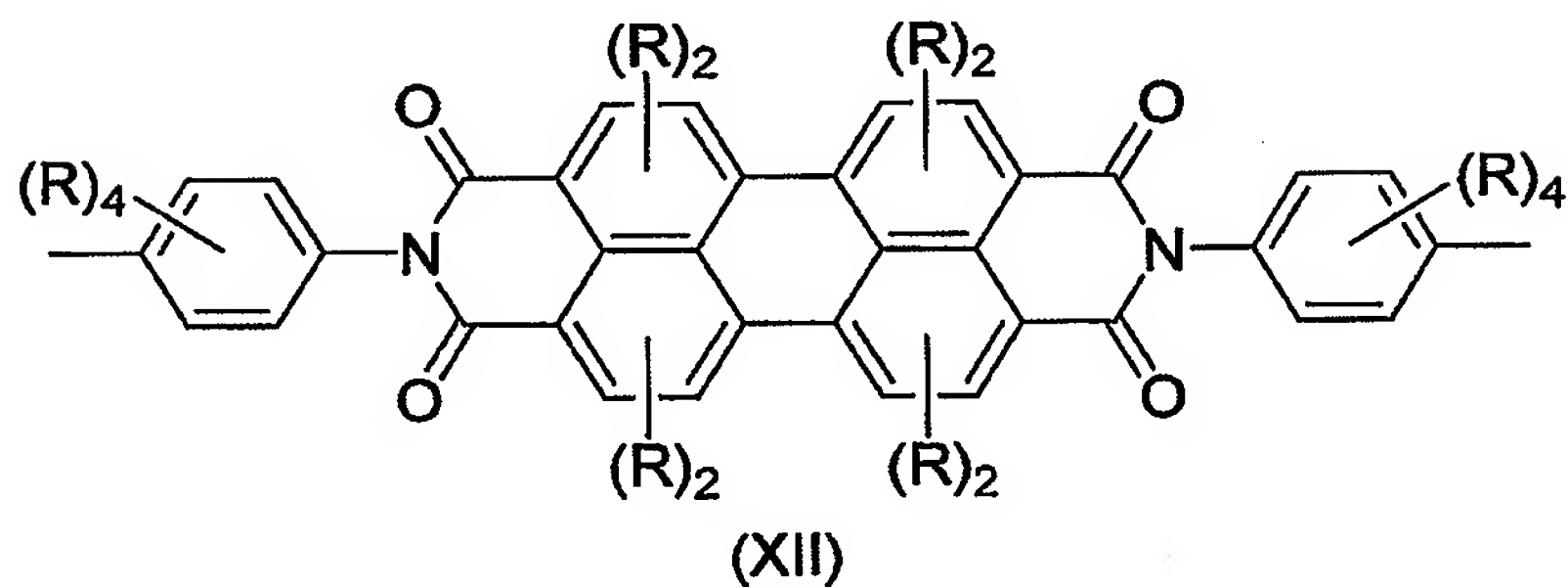
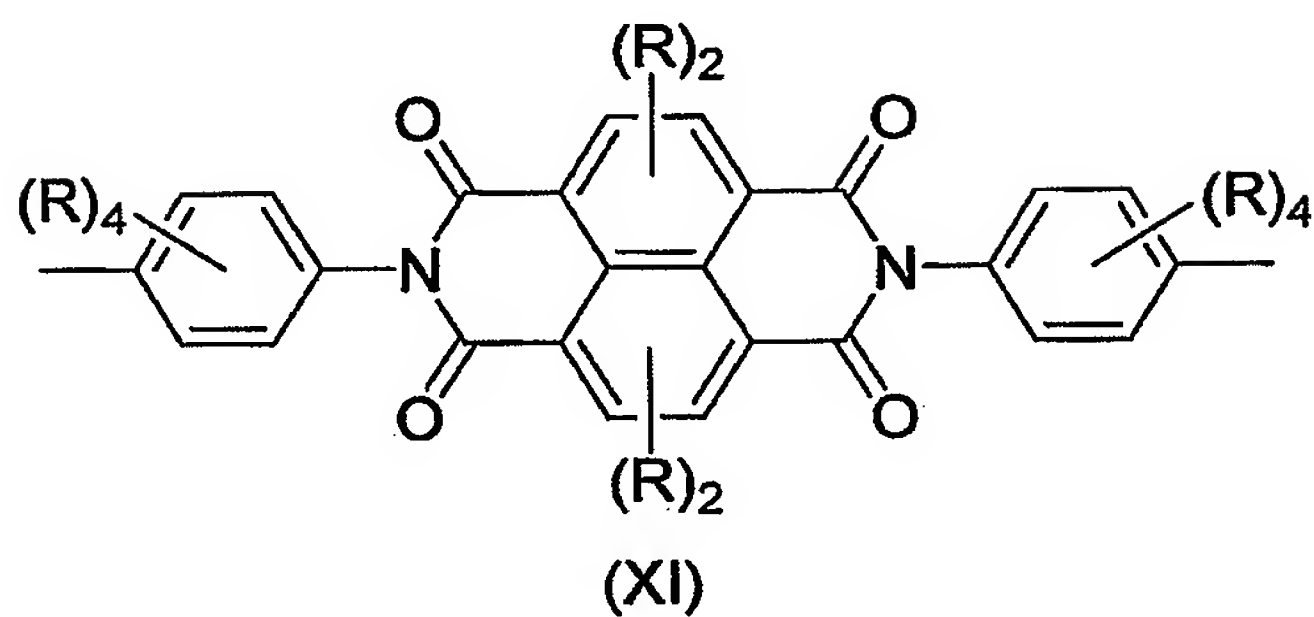
In one embodiment of the invention, the at least one second monomeric unit is selected from (i) aromatic groups having Formula III below; (ii) 6-membered-ring heteroaromatic groups having Formula IV below; (iii) 5-membered-ring heteroaromatic groups having Formula V below; (iv) aromatic groups having Formula VI below; (v) fused ring aromatic groups having Formula VII through Formula XII below; and (vi) combinations thereof,







5



10

where:

in each of Formulae III through XII:

R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub>

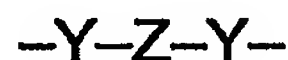
15

- fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring;
- R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl
- in each of Formulae III, IV, V, VI, VII, VIII, IX and X:
- E can be the same or different at each occurrence and is a single bond or a linking group selected from arylene and heteroarylene;
- in Formula V:
- A is independently at each occurrence C or N and  $\gamma$  is 0 or an integer selected from 1 or 2, such that when both A are N, then  $\gamma$  is 0; or when one of A is N and one of A is C, then  $\gamma$  is 1; or when both A are C, then  $\gamma$  is 2;
- Q is O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:
- R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;
- in Formula VI:
- Q<sup>1</sup> is a carbonyl group, O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:
- R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;
- W is H, alkyl or heteroalkyl; or both of W together can represent one single bond;
- in Formula VII:
- the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;
- in Formula VIII:
- the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10- positions;
- in Formula IX:
- a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8 position; and

in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

In one embodiment of the invention, the second monomeric unit  
5 comprises an electron deficient group ("ED unit") and has a formula



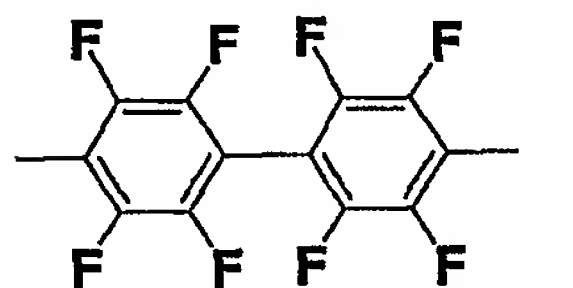
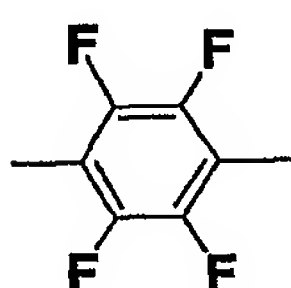
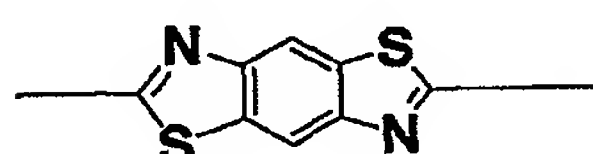
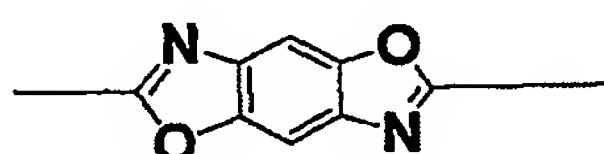
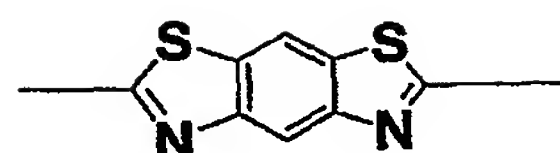
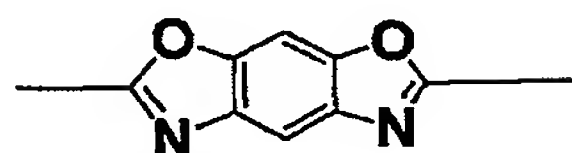
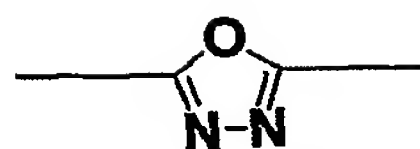
wherein:

10 Y is an aromatic group with at least one substituent selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR<sup>5</sup>,  
R<sup>5</sup> is H or an alkyl; and  
Z is an electron deficient group.

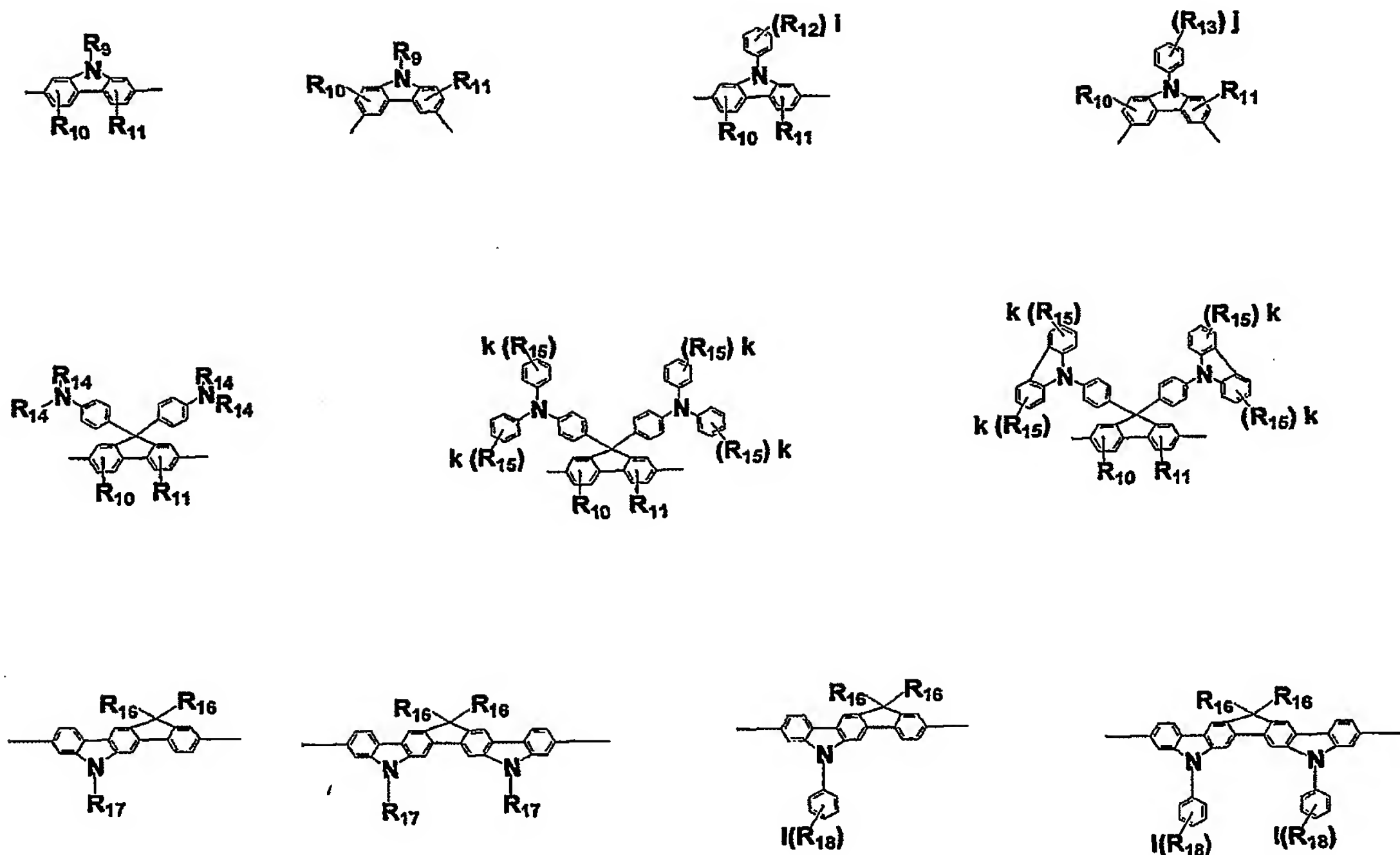
15 Examples of suitable aromatic groups for Y include mono- and polycyclic aromatic hydrocarbons, such as fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and the like. The aromatic group can be substituted at one or more positions, preferably two positions. In one embodiment, the substituents are alkyl  
20 groups having from 1 to 20 carbon atoms. In one embodiment the Y groups are fluorenes with two alkyl groups in the 9-position.

Examples of suitable electron deficient groups for Z include heteroaromatic groups having heteroatoms selected from O, N, and S, and fluorinated aromatic groups. In one embodiment, Z is selected from  
25 oxazole-type, oxadiazole-type, thiazole-type, and fluorinated aromatic groups, such as phenyls and biphenyls.

In one embodiment, the Z group is selected from:



- In one embodiment of the invention, the second monomeric unit is one having hole transport properties ("HT unit"). In general, the HT monomeric unit has an electron rich group. Examples of suitable HT monomeric units include, but are not limited to, carbazoles, triarylamine, and aromatic groups having carbazole or triarylamine groups. Of particular interest as hole-transport monomers are the N-aryl carbazoles with alkyl substituents as they have better solubility and better processibility compared to other hole-transport monomers. Specific examples include:

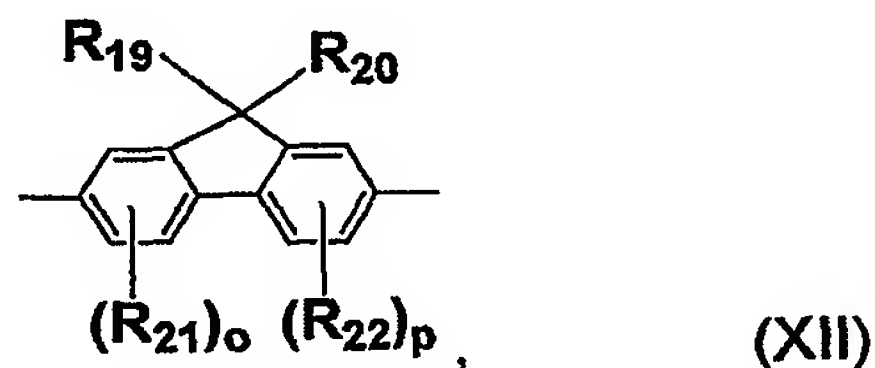


wherein:

R<sub>9</sub>-R<sub>18</sub> are same or different and are selected from alkyl,  
 heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR<sup>5</sup>,  
 R<sup>5</sup> is H or an alkyl;

i, j, k, l are numbers of substituents on the benzene rings and are  
 same or different and each of i, j, k, and l is in a range of 0-3.

In one embodiment of the invention, the second monomeric unit is  
 one which enhances the solubility of the resulting polymer ("SE unit").  
 Examples of suitable SE monomeric units include, but are not limited to,  
 substituted fluorenes, substituted phenyls, substituted biphenyls, and  
 substituted bridged biphenyls. In one embodiment, the SE monomeric unit  
 has Formula XII below:



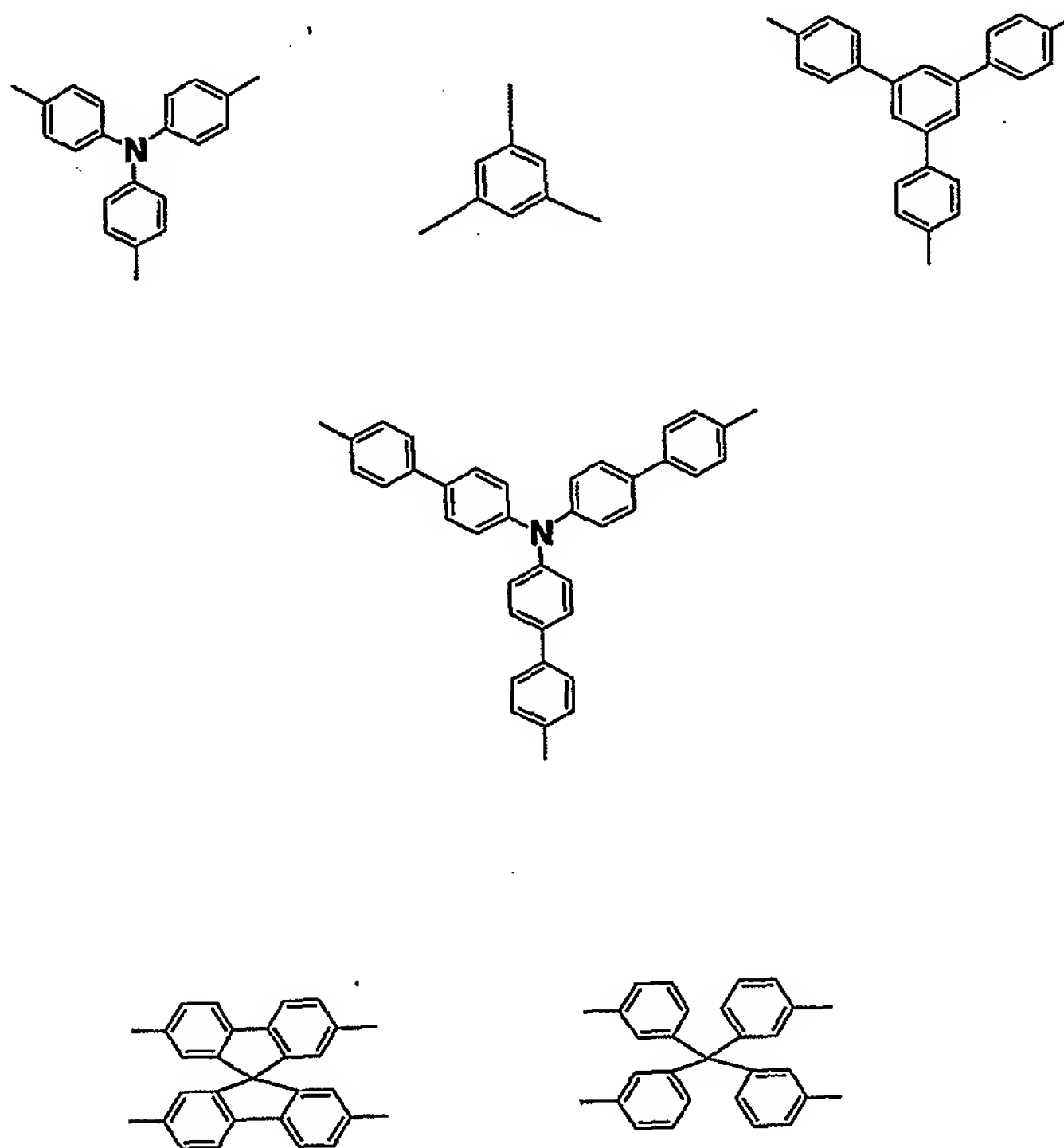
wherein

R<sub>19</sub>-R<sub>22</sub> are same or different and are selected from alkyl,  
 heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and N R<sup>5</sup>,  
 R<sup>5</sup> is H or an alkyl; and

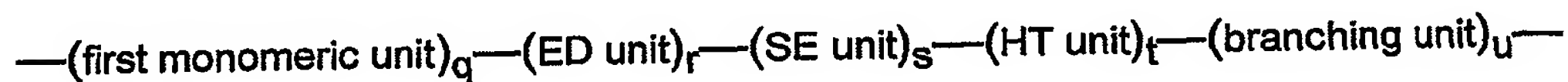


o and p are numbers of substituents on the benzene rings and are same or different and each of o and p is in a range of 0-3.

In one embodiment of the invention, the second monomeric unit is a branching monomeric unit having more than two linkage sites. Examples of suitable branching monomeric units include, but are not limited to:



In the copolymer of the invention, more than one of the second monomeric unit can be present with the first monomeric unit. For example, the copolymer can have the formula



wherein:

the first monomeric unit has Formula I as described above;

the ED, SE, HT, and branching units are as defined above;

q is an integer; and

r, s, t, and u are 0 or an integer, with the proviso that at least one of

r, s, t, and u is an integer.

The relative molar proportion of first monomeric unit to the at least one second monomeric unit(s) can be from 99.9:0.1 to 1:99 or 99.5:0.5 to 10:90; alternatively 99:1 to 20:80, and further alternatively 99:1 to 50:50.

The incorporation of the monomers in the formation of the polymer can be random or controlled, resulting in copolymers which include, but are not limited to, random copolymers, alternating copolymers and block copolymers.

5       The copolymers of the invention, generally comprise at least 3 first monomeric units. In one embodiment, the copolymer comprises at least 10 first monomeric units. In one embodiment, the copolymer comprises at least 50 first monomeric units.

10       In the copolymers of the invention, the degree of polymerization is generally at least 5. In one embodiment, the degree of polymerization is at least 10. In one embodiment, the degree of polymerization is at least 50.

#### Synthesis

15       The copolymers of the invention can generally be prepared by three known synthetic routes. In the first synthetic method, as described in Yamamoto, *Progress in Polymer Science*, Vol. 17, p 1153 (1992), the dihalo derivatives of the monomeric units are reacted with a stoichiometric amount of a zerovalent nickel compound, such as bis(1,5-cyclooctadiene)nickel(0). In the second method, as described in Colon et al., *Journal of Polymer Science, Part A, Polymer chemistry Edition*, Vol. 28, p. 367 (1990). The dihalo derivatives of the monomeric units are reacted with catalytic amounts of Ni(II) compounds in the presence of stoichiometric amounts of a material capable of reducing the divalent nickel ion to zerovalent nickel. Suitable materials include zinc, 20       magnesium, calcium and lithium. In the third synthetic method, as described in US Patent 5,962,631, and published PCT application WO 00/53565, a dihalo derivative of one monomeric unit is reacted with a derivative of another monomeric unit having two reactive groups selected from boronic acid, boronic acid esters, and boranes, in the presence of a zerovalent palladium catalyst, such as tetrakis(triphenylphosphine)Pd. 30       The di-tosylate derivatives of the monomeric units can also be used.

35       In some embodiments of the invention, the copolymer can be reacted with an end-capping compound to convert the reactive end group to a non-reactive end group. The end-capping compound is generally added to a preformed polymer and ends the polymerization reaction. The end-capping compound is generally an aromatic compound having a single reactive group, such as an aromatic ring having a single halide group or boronic acid or ester group. Examples of suitable end-capping

compounds include 9-bromoanthracene, 4-bromo-1,2-dimethoxybenzene, 1-bromopyrene, iodobenzene, bromobenzene, 2-bromo-9-fluorenone, and benzenboronic acid. The end-capping group may also be designed to add functionality, such as charge transport properties and color shifting. It may also affect interchain aggregation.

The copolymers of the invention can be used in electronic devices. FIG. 1 illustrates an exemplary electronic device 100 that includes an active layer positioned between two electrical contact layers. The electronic device 100 includes a hole transport layer 120 located between the active layer 130 and an anode layer 110. An optional electron transport layer 140 is located between the active layer 130 and a cathode layer 150. Depending on the application of the device 100, the active layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, phototubes, and photovoltaic cells, as described in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc., 1966). The device is not limited with respect to system, driving method, and utility mode. The polymers may be used as part of an organic active layer, hole-transport layer, or electron-transport layer in an organic light-emitting diode ("OLED") of a display. When used in OLEDs, some of the best device performances to date including high efficiency and blue color purity have been achieved.

The device may include a support or substrate (not shown) that can be adjacent to the anode layer 110 or the cathode layer 150. Most frequently, the support is adjacent the anode layer 110. The support can be flexible or rigid, organic or inorganic. Generally, glass or flexible organic films are used as a support. The anode layer 110 is an electrode that is more efficient for injecting holes compared to the cathode layer 150. The anode can include materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode layer 110 is to be light transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, may be used. Some non-limiting, specific examples of materials for anode layer 110 include indium-tin-oxide ("ITO"), aluminum-tin-oxide, gold, silver,

copper, nickel, and selenium. The anode may also comprise an organic material such as polyaniline.

The anode layer 110 may be formed by a chemical or physical vapor deposition process or spin-cast process. Chemical vapor deposition  
5 may be performed as a plasma-enhanced chemical vapor deposition ("PECVD") or metal organic chemical vapor deposition ("MOCVD"). Physical vapor deposition can include all forms of sputtering, including ion beam sputtering, as e-beam evaporation and resistance evaporation. Specific forms of physical vapor deposition include rf magnetron sputtering  
10 or inductively-coupled plasma physical vapor deposition ("IMP-PVD"). These deposition techniques are well known within the semiconductor fabrication arts.

Examples of materials which may facilitate hole-injection/transport comprise N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-  
15 diamine (TPD) and bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP); hole-transport polymers such as polyvinylcarbazole (PVK), (phenylmethyl)polysilane, poly(3,4-ethylenedioxythiophene) (PEDOT), and polyaniline (PANI), or the like; electron and hole-transporting materials such as 4,4'-N,N'-dicarbazole  
20 biphenyl (BCP); or light-emitting materials with good hole-transport properties such as chelated oxinoid compounds, including tris(8-hydroxyquinolato)aluminum (Alq<sub>3</sub>) or the like. In some embodiments, if the conductivity of the hole-injection/transport layer 120 can be made similar to anode layer 110, the anode layer 110 may not be  
25 required and the hole-injection/transport layer 120 can act as the anode for the electronic device.

The hole-injection/transport layer 120 can be formed using any conventional means, including spin-coating, casting, and printing, such as gravure printing. The layer can also be applied by ink jet printing, thermal  
30 patterning, or chemical or physical vapor deposition.

Usually, the anode layer 110 and the hole-injection/transport layer 120 are patterned during the same lithographic operation. The pattern may vary as desired. The layers can be formed in a pattern by, for example, positioning a patterned mask or resist on the first flexible  
35 composite barrier structure prior to applying the first electrical contact layer material. Alternatively, the layers can be applied as an overall layer (also called blanket deposit) and subsequently patterned using, for example, a patterned resist layer and wet chemical or dry etching techniques. Other



processes for patterning that are well known in the art can also be used. When the electronic devices are located within an array, the anode layer 110 and hole-injection/transport layer 120 typically are formed into substantially parallel strips having lengths that extend in substantially the same direction.

The polymers of the invention have particular utility in the active layer 130. This layer can be applied from solutions by any conventional technique, including spin-coating, casting, and printing.

Optional layer 140 can function both to facilitate electron-injection/transport, and also serve as a buffer layer or confinement layer to prevent quenching reactions at layer interfaces. More specifically, layer 140 may promote electron mobility and reduce the likelihood of a quenching reaction if layers 130 and 150 would otherwise be in direct contact.

Examples of materials which may facilitate hole-injection/transport comprise metal-chelated oxinoid compounds (e.g., Alq<sub>3</sub> or the like); phenanthroline-based compounds (e.g., 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ("DDPA"), 4,7-diphenyl-1,10-phenanthroline ("DPA"), or the like); azole compounds (e.g., 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole ("PBD" or the like), 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole ("TAZ" or the like); other similar compounds; or any one or more combinations thereof. Alternatively, optional layer 140 may be inorganic and comprise BaO, LiF, Li<sub>2</sub>O, or the like.

The electron-injection/transport layer 140 can be formed using any conventional means, including spin-coating, casting, and printing. The layer can also be applied by ink jet printing, thermal patterning, or chemical or physical vapor deposition.

The cathode layer 150 is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode layer 150 can be any metal or nonmetal having a lower work function than the first electrical contact layer (in this case, the anode layer 110). Materials for the second electrical contact layer can be selected from alkali metals of Group 1 (e.g., Li, Na, K, Rb, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, the rare earths, the lanthanides (e.g., Ce, Sm, Eu, or the like), and the actinides. Materials such as aluminum, indium, calcium, barium, yttrium, and magnesium, and combinations, may also be used. Specific non-limiting examples of materials for the cathode layer 150



include barium, lithium, cerium, cesium, europium, rubidium, yttrium, magnesium, and samarium.

The cathode layer 150 is usually formed by a chemical or physical vapor deposition process. In general, the cathode layer will be patterned, as discussed above in reference to the anode layer 110 and optional conductive polymer layer 120. If the device lies within an array, the cathode layer 150 may be patterned into substantially parallel strips, where the lengths of the cathode layer strips extend in substantially the same direction and substantially perpendicular to the lengths of the anode layer strips. Electronic elements called pixels are formed at the cross points (where an anode layer strip intersects a cathode layer strip when the array is seen from a plan or top view).

In other embodiments, additional layer(s) may be present within organic electronic devices. For example, a layer (not shown) between the conductive polymer layer 120 and the active layer 130 may facilitate positive charge transport, band-gap matching of the layers, function as a protective layer, or the like. Similarly, additional layers (not shown) between the active layer 130 and the cathode layer 150 may facilitate negative charge transport, band-gap matching between the layers, function as a protective layer, or the like. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 110, the conductive polymer layer 120, the active layer 130, and cathode layer 150, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers may be determined by balancing the goals of providing a device with high device efficiency with the cost of manufacturing, manufacturing complexities, or potentially other factors.

Although not meant to limit, the different layers may have the following range of thicknesses: inorganic anode layer 110, usually no greater than approximately 500 nm, for example, approximately 10-200 nm; conductive polymer layer 120, usually no greater than approximately 250 nm, for example, approximately 20-200 nm; active layer 130, usually no greater than approximately 1000 nm, for example, approximately 10-80 nm; optional layer 140, usually no greater than approximately 100 nm, for example, approximately 20-80 nm; and cathode layer 150, usually no greater than approximately 100 nm, for example, approximately 30-500 nm. If the anode layer 110 or the cathode layer 150

needs to transmit at least some light, the thickness of such layer may not exceed approximately 100 nm.

In polymer light emitting diodes, electrons and holes, injected from the cathode 150 and anode 110 layers, respectively into the active polymer layer 130, form negative and positively charged polarons in the polymer. These polarons migrate under the influence of the applied electric field, forming a polaron exciton with an oppositely charged species and subsequently undergoing radiative recombination. A sufficient potential difference between the anode and cathode, usually less than approximately 12 volts, and in many instances no greater than approximately 5 volts, may be applied to the device. The actual potential difference may depend on the use of the device in a larger electronic component. In many embodiments, the anode layer 110 is biased to a positive voltage and the cathode layer 150 is at substantially ground potential or zero volts during the operation of the electronic device. A battery or other power source(s) may be electrically connected to the electronic device as part of a circuit but is not illustrated in FIG. 1.

The invention will now be described in greater detail by reference to the following non-limiting examples.

20

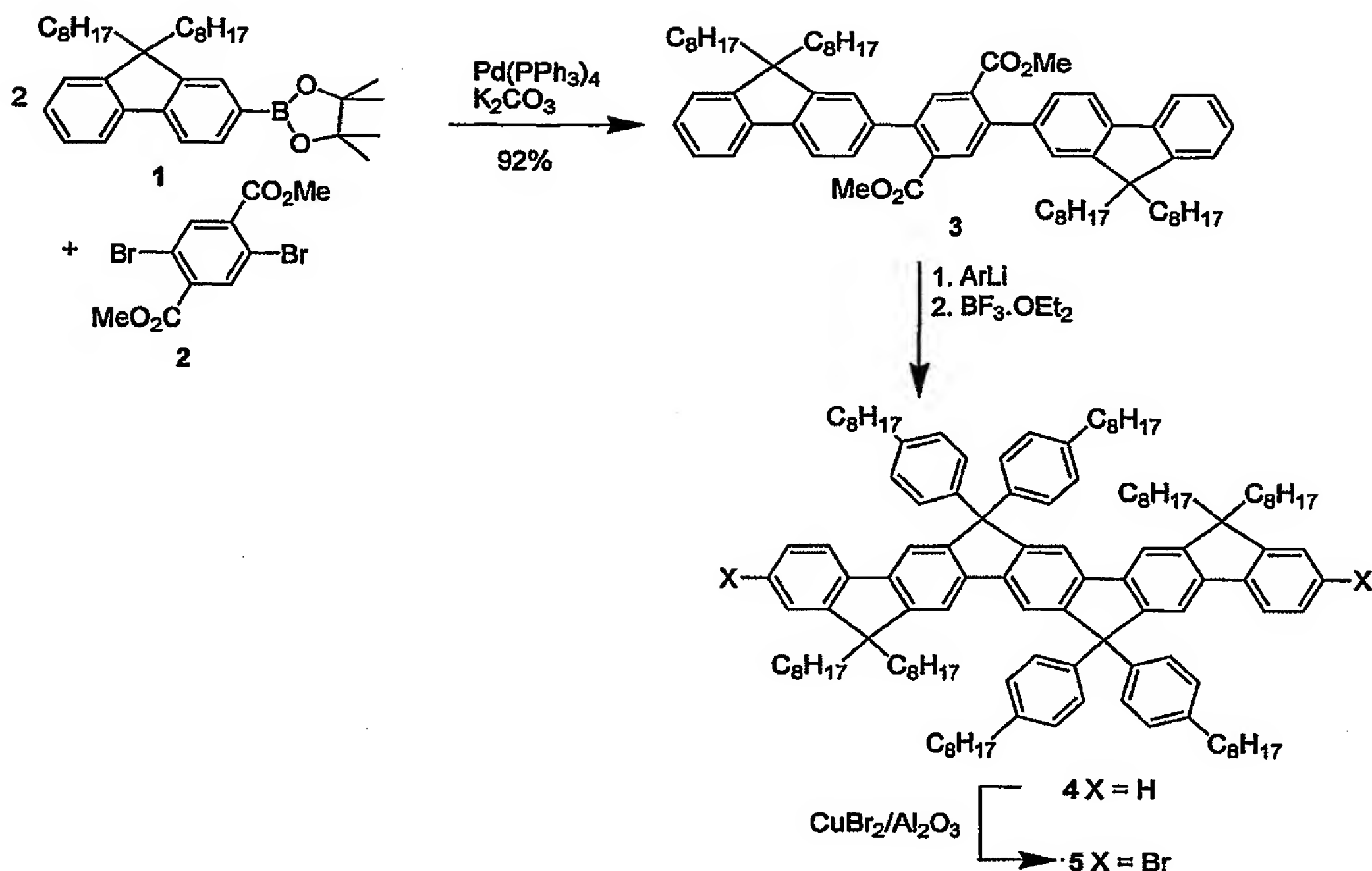
### EXAMPLES

#### Example 1

This example illustrates the preparation of a first monomer which can be used to prepare a copolymer of the invention..

As shown in the scheme below, Suzuki coupling of the fluorene-2-boronate ester **1**, with the dibromoterephthalate **2** generated an intermediate, the pentaphenylenediester **3** in 92 % yield. Addition of an excess of 4-alkylphenyl lithium produced a diol which was facilely ring-closed using  $\text{BF}_3$  etherate to generate the ladder-type pentaphenylene **4** (95 %). Bromination of **4** using  $\text{CuBr}_2$  on alumina<sup>23</sup> gave the monomer **5** (91 %).

30



### Synthesis of the pentaphenylene diester **3**.

The boronate ester **1** (4.65 g, 9.0 mmol), diester **2** (1.52 g, 4.39 mmol),  $\text{K}_2\text{CO}_3$  (1.21 g, 8.8 mmol) were dissolved in THF (40 mL) and water (20 mL) in a 100 mL schlenk flask. The solution was purged with argon for twenty minutes and then tetrakis(triphenylphosphine)palladium (152 mg, 0.03 equiv) was added and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and after 16 h was worked up. The cooled mixture was extracted with diethyl ether, and the extract was washed with saturated salt and then dried over  $\text{MgSO}_4$ . The crude product so obtained was purified by chromatography on silica using 0-5 % ethylacetate in hexane as eluent. The product **3** was isolated as a thick viscous oil (3.94 g, 92 %).  $^1\text{H}$  NMR: ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.88 (s, 2H) 7.78 (m, 4H) 7.40-7.33 (m, 10H) 3.65 (s, 6H) 2.00 (t, 8H,  $J = 8.5\text{Hz}$ ) 1.21-1.07 (m, 40H) 0.62-0.83 (m, 20H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  169.26, 151.74, 151.62, 141.89, 141.56, 141.43, 139.54, 134.37, 132.44, 128.02, 127.82, 127.59, 123.84, 123.73, 120.55, 120.29, 55.96, 52.78, 41.16, 32.54, 30.81, 30.05, 29.99, 24.56, 23.35, 14.58 ppm. FDMS:  $m/z$  971.3 Elemental Analysis: Calculated C 84.07 H 9.34 Found C 84.12 H 9.32.

Synthesis of the ladder-type pentaphenylene 4.

a) A solution of 4-octylbromobenzene (3.05 mL, 3.4 g, 12.6 mmol) in dry THF (40 mL) in a 250 mL schlenk flask, was cooled to -78 °C in an acetone/dry ice bath. n-Butyllithium in hexane (8.0 mL, 1.6 M, 12.8 mmol) was then added and stirred for 20 minutes. Then a solution of the diester 5 (2.05 g, 2.1 mmol) in dry THF (40 mL) was added dropwise with stirring and the solution was slowly allowed to warm to room temperature. The mixture was stirred overnight and then the quenched with brine. The mixture was extracted with diethyl ether, and the extract was washed with salt and dried over MgSO<sub>4</sub>. The crude product was chromatographed on silica using 0-5 % ethylacetate in hexane as eluent to give the diol as a thick viscous oil. (3.39 g, 96 %). <sup>1</sup>H NMR: δ 7.61 (m, 2H) 7.45 (d, 2H, J = 7.6Hz) 7.29 (m, 6H) 7.12 (m, 16H) 6.76 (m, 4H) 6.69 (s, 2H) 3.11 (s, 2H) 2.61 (t, 8H, J = 7.6Hz) 1.77-0.45 (m, 128H) ppm. <sup>13</sup>C NMR: δ 151.63, 151.23, 146.41, 144.19, 142.74, 141.71, 141.21, 141.05, 139.29, 136.29, 129.29, 128.76, 128.58, 127.93, 127.48, 124.32, 123.63, 120.35, 120.22, 83.91, 55.75, 40.55, 36.30, 32.72, 32.60, 32.45, 30.73, 30.30, 30.12, 30.09, 30.07, 30.04, 24.56, 23.46, 23.39, 14.65, 14.61 ppm. FDMS: m/z 1668.3.

b) ring-closure: The diol (3.30 g, 1.98 mmol) was dissolved in dichloromethane (30 mL, used as purchased) and BF<sub>3</sub> etherate (0.20 mL) was added with stirring at room temperature. The colorless solution turned deep brown immediately upon addition and became light yellow within minutes. After 10 minutes, methanol (50 mL) was added to the solution whereupon the pentamer 4 started to precipitate as a colourless solid. The mixture was stirred for 12 h and then the solid was collected by filtration, washed with methanol and dried. The product was redissolved in dichloromethane and precipitated again by addition of methanol. Isolated yield of 4 = 3.06 g (95 %). <sup>1</sup>H NMR: δ 7.83 (s, 2H) 7.63 (m, 6H) 7.33-7.11 (m, 22H) 2.58 (t, 8H, J = 7.6Hz) 2.02 /t, 3H, J = 7.9Hz) 1.63-0.62 (m, 120H) ppm. <sup>13</sup>C NMR: δ 152.80, 152.05, 151.88, 151.55, 144.35, 142.29, 141.83, 140.91, 140.87, 140.25, 129.11, 128.97, 127.63, 127.37, 123.65, 120.34, 118.16, 117.82, 115.35, 65.15, 55.61, 41.39, 36.28, 32.65, 32.55, 32.30, 30.82, 30.30, 30.22, 30.03, 30.01, 29.98, 24.67, 23.43, 23.34, 14.64, 14.60 ppm. FDMS: m/z 1633.2 . Elemental Analysis: Calculated C 89.75 H 10.25 %; Found: C 89.77 H 10.19 %.



### Synthesis of monomer 5.

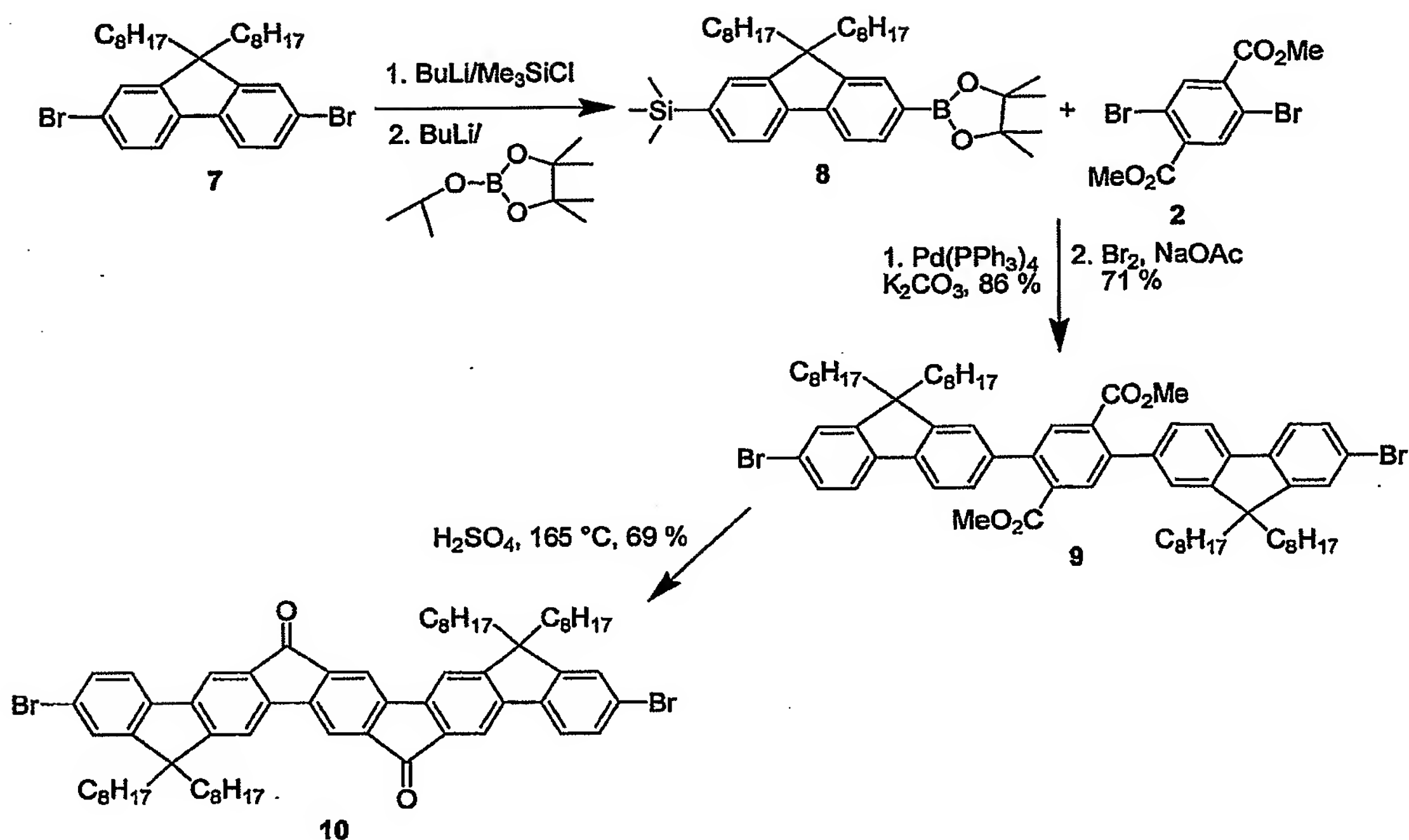
The pentaphenylene 4 (0.80 g, 0.49 mmol) was added to carbon tetrachloride (30 mL) in a 100 mL round-bottomed flask, followed by CuBr<sub>2</sub> on alumina (2.0 g).<sup>23</sup> The reaction was heated under reflux with stirring and monitored by FDMS, which showed nearly quantitative formation of the dibromide after 14 h. The reaction mixture was concentrated, and the residue was loaded on silica and chromatographed on silica using hexane as eluent. The product 5 was isolated as a light yellow solid, (0.80 g, 91 %). <sup>1</sup>H NMR:  $\delta$  7.82 (s, 2H) 7.66 (d, 4H, J = 9.1Hz) 7.42 (m, 6H) 7.24 (d, 8H, J = 8.2Hz) 7.12 (d, 8H, J = 8.2Hz) 2.58 (t, 8H, J = 7.3Hz) 2.00 (t, 8H, J = 7.6Hz) 1.59 (m, 8H) 1.31-0.78 (m, 112H) ppm. <sup>13</sup>C NMR:  $\delta$  154.19, 152.90, 152.30, 151.23, 144.17, 142.38, 140.97, 140.85, 140.76, 140.69, 130.52, 129.14, 128.95, 126.92, 121.79, 121.51, 118.29, 117.97, 115.44, 65.17, 55.99, 41.28, 36.26, 32.65, 32.53, 32.29, 30.73, 30.69, 30.29, 30.22, 30.00, 29.97, 24.62, 23.43, 23.35, 14.64, 14.60 ppm. FDMS: m/z 1780.50. Elemental Analysis: Calculated C 81.84 H 9.23 %; Found: 81.99 H 9.24 %.

### Example 3

This example illustrates the preparation of a second monomer which can be used to form the copolymer of the invention.

As shown in the scheme below, 2,7-Dibromo-9,9-dioctylfluorene 7 was converted via the monosilyl compound to the boronate 8. Suzuki coupling of this with the terephthalate 2 gave a crude disilylpentaphenylene in 86 % yield, which was converted to the dibromide 9 with sodium acetate and bromine (72 %). The monomers 5 could then be obtained by addition of aryllithium and ring closure, but in view of the longer synthesis and lower overall yield, this route is inferior to the previously described route. Treatment of 9 with concentrated sulphuric acid at 165 °C induced a double intramolecular Friedel-Crafts acylation to produce the desired diketone 10 in 65 % yield. By contrast treatment of the unbrominated diester 3 under the same condition gave incomplete ring closure.





#### Synthesis of 7-trimethylsilyl-9,9-di-n-octylfluorene-2-boronate 8.

- 5 n-Butyllithium in hexane (6.0 mL, 1.6 M, 9.6 mmol) was added to a solution of 2,7-dibromo-9,9-di-n-octylfluorene (7) (5.00 g, 9.13 mmol) in dry THF (50 mL) in a schlenk flask at -78 °C and the mixture was stirred for 20 minutes. Then chlorotrimethylsilane (1.5 mL, 1.29 g, 1.3 equiv) was added and the reaction was allowed to slowly warm to room temperature.
- 10 The mixture was stirred overnight and the reaction was quenched with saturated brine. The product was extracted into diethyl ether, and the extract was washed with brine and dried over MgSO<sub>4</sub>. The crude product was chromatographed on silica using hexane as eluent to give 2-bromo-7-trimethylsilyl-9,9-di-n-octylfluorene as a colourless oil, (3.50 g, 71 %).
- 15 n-Butyllithium in hexane (4.4 mL, 1.6 M, mmol) was added to a solution of 2-bromo-7-trimethylsilyl-9,9-di-n-octylfluorene (3.47 g, 6.41 mmol) in dry THF (75 mL) in a schlenk flask at -78 °C, and the mixture was stirred for 20 minutes. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.44 mL, 1.31 g, 7.04 mmol) was added and the reaction was stirred for
- 20 24 h after warming to room temperature. The reaction was then quenched with brine, and the product was extracted into diethyl ether. The extract was washed with brine and dried over MgSO<sub>4</sub>. The crude product was

chromatographed on silica using 0-3 % ethylacetate in hexane as eluent, to give **8** as a colourless solid (2.67 g, 71 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.73 (m, 4H) 7.51 (m, 2H) 1.99 (t, 4H,  $J = 8.2\text{Hz}$ ) 1.36-0.54 (m, 42H) 0.31 (s, 9H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  151.60, 151.34, 149.76, 145.29, 142.69, 141.07, 134.71, 133.01, 130.08, 129.03, 120.50, 120.25, 84.93, 56.22, 41.26, 33.01, 32.84, 31.11, 30.37, 25.98, 24.95, 23.85, 15.08, 0.01. FDMS  $m/z$  588.90.

#### Synthesis of dibromopentaphenylene **9**.

The boronate ester **8** (2.45 g, 4.16 mmol), the diester **9** (697 mg, 1.98 mmol), and  $\text{K}_2\text{CO}_3$  (821 mg) were dissolved in a mixture of THF (20 mL) and  $\text{H}_2\text{O}$  (10 mL) in a schlenk flask and the mixture was purged with argon for 20 minutes. To this tetrakis(triphenylphosphine)palladium (114 mg, 0.05 equiv) was added and the mixture was heated at  $85^\circ\text{C}$  for 20 h. The cooled mixture was extracted with diethyl ether, and the extract was washed with brine and dried over  $\text{MgSO}_4$ . The residue was chromatographed on silica using 0-3 % ethylacetate in hexane to give the crude disilylpentaphenylene (1.89 g, 86 %).

In a schlenk flask, the diester **2** (1.89 g, 1.69 mmol) was added to dry THF (34 mL) along with anhydrous sodium acetate (278 mg, 2 equiv) and cooled to  $0^\circ\text{C}$ . Bromine (0.37 mL, 1.15 g, 4.2 equiv) was added and the mixture was stirred for 20 minutes. The reaction was quenched by addition of triethylamine (1.89 mL, 8 equiv) followed by an excess of aqueous  $\text{Na}_2\text{SO}_3$ . The product was extracted into diethyl ether, and the extract was washed with sodium sulfite solution and dried over  $\text{MgSO}_4$ . The residue was recrystallized from hot hexane to give the dibromide **9** as shiny colourless crystals (1.37 g, 72 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.87 (s, 2H) 7.77 (d, 2H,  $J = 7.9\text{Hz}$ ) 7.64 (d, 2H,  $J = 7.9\text{Hz}$ ) 7.53-7.31 (m, 8H) 3.64 (s, 6H) 1.99 (t, 8H,  $J = 8.8\text{Hz}$ ) 1.27-0.62 (m, 60H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  169.06, 154.06, 151.27, 141.89, 140.58, 140.49, 140.05, 134.32, 132.51, 130.76, 128.06, 127.04, 123.87, 122.01, 121.96, 120.46, 56.36, 52.82, 41.08, 32.54, 30.74, 30.03, 29.99, 24.52, 23.36, 14.59 ppm. FDMS  $m/z$  1129.30  
Elemental Analysis: Calculated C 72.33 H 7.85 %; Found C 72.75 H 7.91 %.

#### Synthesis of dibromopentaphenylenedione **10**.

The dibromide **9** (1.37 g) was added to 40 mL of 80 %  $\text{H}_2\text{SO}_4$  (made from 4 mL  $\text{H}_2\text{O}$  and 36 mL conc.  $\text{H}_2\text{SO}_4$ ) and heated with stirring at  $165^\circ\text{C}$  for 3h during which time the white solid turned brown. The acid was decanted off and the product was extracted into dichloromethane, and

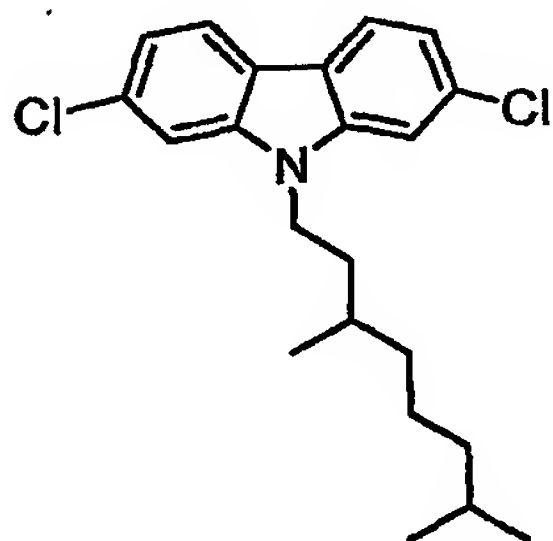
the extract was washed with sodium hydrogencarbonate solution and dried over  $\text{MgSO}_4$ . The crude product was purified by chromatography on silica using 0-3 % ethylacetate in hexane as eluent to give the diketone 10 as a grey solid (0.88 g, 69 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.97 (s, 2H) 7.86 (s, 2H) 7.65-7.49 (m, 8H) 2.03 (t, 8H,  $J = 8.5\text{Hz}$ ) 1.25-0.62 (m, 60H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  192.91, 159.79, 153.77, 146.79, 144.19, 142.53, 140.81, 139.69, 134.70, 131.11, 127.10, 122.66, 122.21, 116.50, 116.38, 116.27, 56.96, 40.88, 32.53, 30.66, 29.97, 29.95, 24.60, 23.37, 14.60 ppm. Elemental Analysis: Calculated C 74.42 H 7.57 %; Found C 74.63 H 7.60 %.

#### Example 4

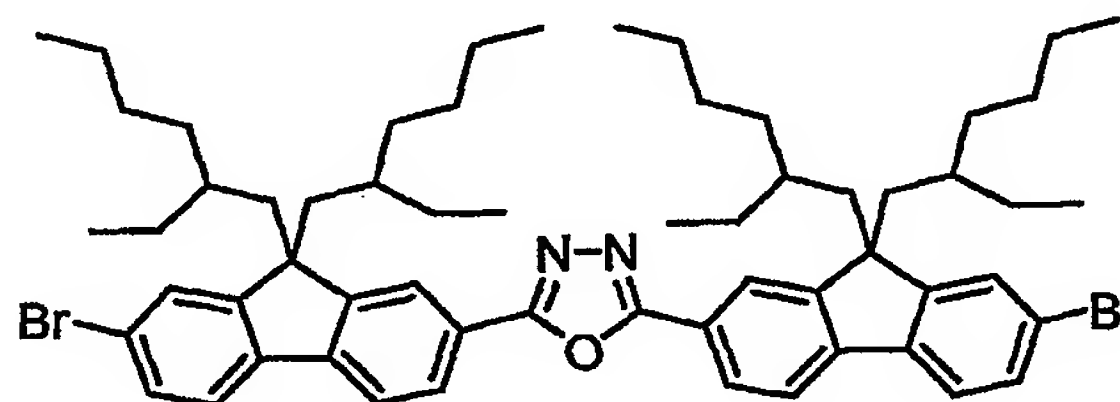
This example illustrates the preparation of a copolymer of the invention.

Comonomers:

Monomer 5 40 mol%



20 mol%



40 mol%

Under inert conditions, DMF (7 mL) will be added to a Schlenk tube equipped with a stirring bar and containing *bis*(1,5-cyclooctadiene)nickel (0) (1.612 g, 5.86 mmol), 2,2'-bipyridyl (0.915 g, 5.86 mmol), and 1,5-cyclooctadiene (0.634 g, 5.86 mmol). The ensuing deep blue/purple solution will be stirred at 60 °C for 30 minutes, and then a solution of monomer 5 from Example 2 (2.065 g, 1.16 mmol), a second monomer, 2,5-bis-[7-bromo-9,9-bis-(2-ethyl-hexyl)-9H-fluoren-2-yl]-[1,3,4]oxadiazole (1.166 g, 1.16 mmol) a third monomer and 2,7-dichloro-9-(3,7-dimethyl-octyl)-9H-carbazole (0.218 g, 0.58 mmol) in toluene (28 mL) will be added via syringe. The reaction mixture will then be stirred at 75 °C for 24 h. The mixture will be cooled to room temperature and

precipitated into a solution of methanol (100 mL), acetone (100 mL) and concentrated hydrochloric acid (5 mL). After stirring for 2 hours, the mixture will be filtered. The solid residue will then be dissolved in chloroform, and again precipitated into a solution of methanol (100 mL),  
5 acetone (100 mL) and concentrated hydrochloric acid (5 mL). After stirring for 1 hour, the mixture will be filtered. The solid will again be dissolved in chloroform and precipitated in pure methanol. Finally the residue will be successively washed with methanol, water and methanol and dried in vacuo.

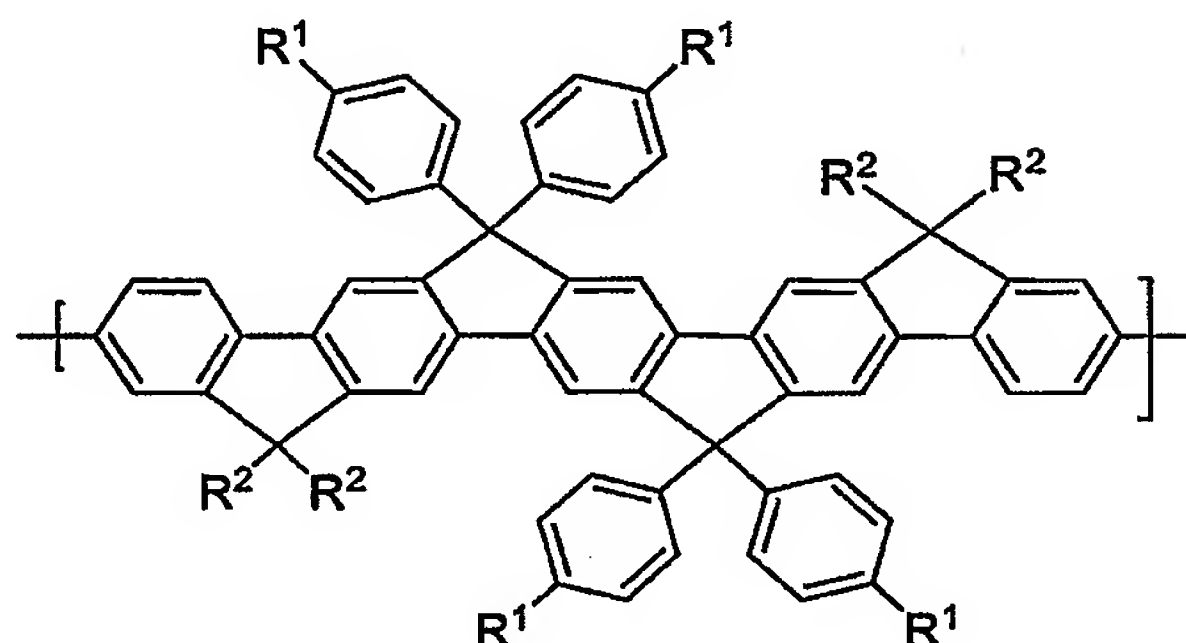
10

CLAIMS

What is claimed is:

1. A copolymer comprising at least one monomeric unit having  
Formula I:

5



(I)

wherein:

R<sup>1</sup> is the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

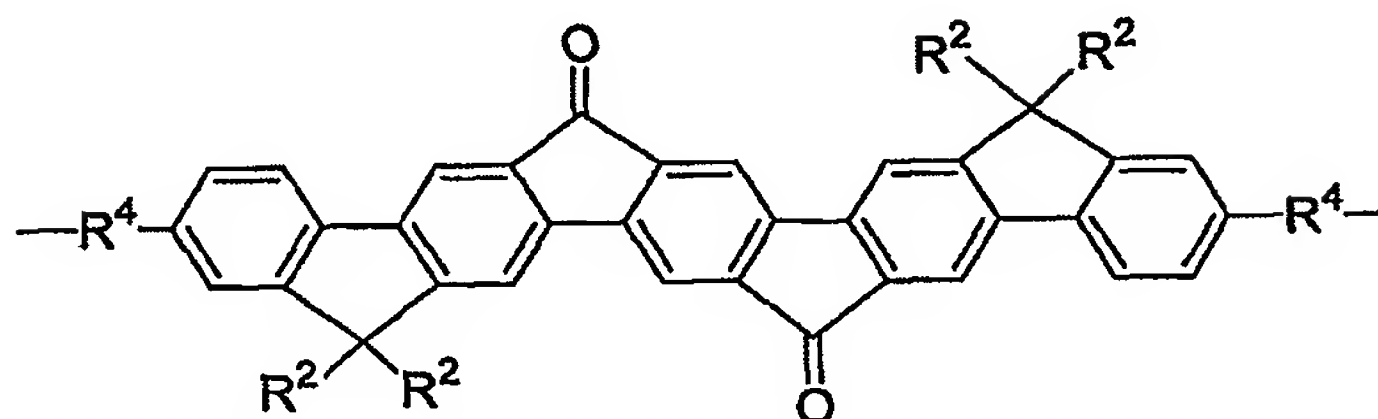
R<sup>2</sup> is the same or different at each occurrence and is selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

and at least one second monomeric unit comprising an aromatic group.



2. A copolymer according to Claim 1, wherein the second monomeric unit has Formula II:



5

(II)

wherein:

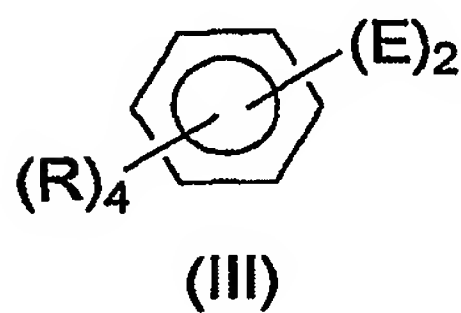
$R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl,  $-CN$ ,  $-OR^3$ ,  $-CO_2R^3$ ,  $-SR^3$ ,  $-N(R^3)_2$ ,  $-P(R^3)_2$ ,  $-SOR^3$ ,  $-SO_2R^3$ , and  $-NO_2$ ; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

15

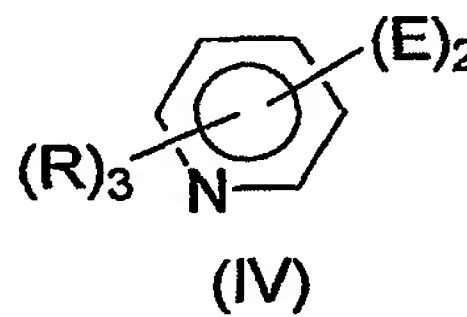
$R^4$  is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

3. A copolymer according to Claim 1, wherein the second monomeric unit has a formula selected from Formula III through Formula XII and combinations thereof,

20

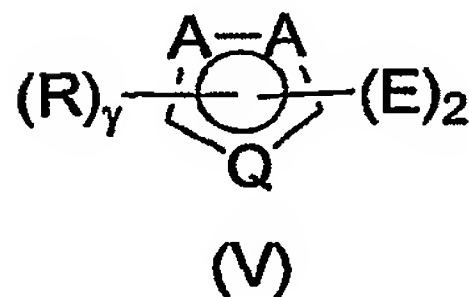


(III)

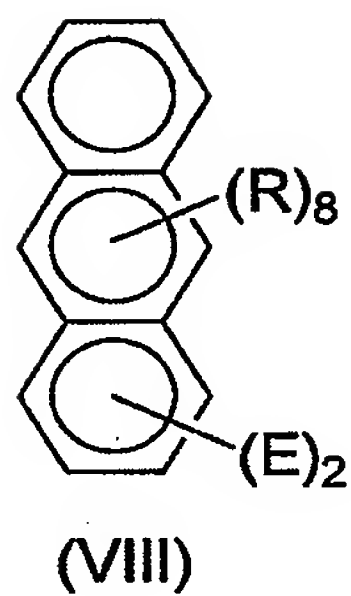
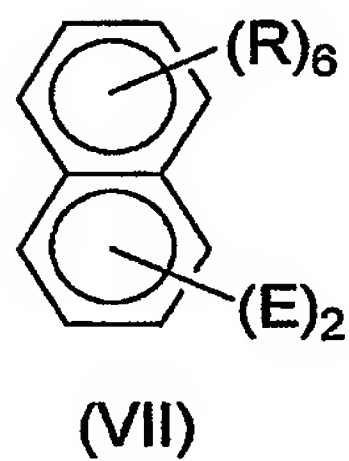
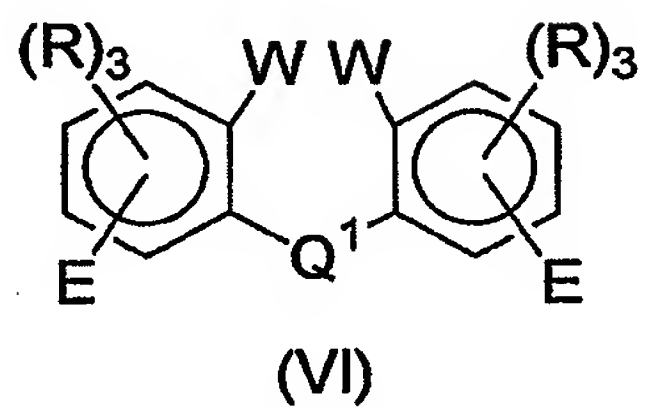


(IV)

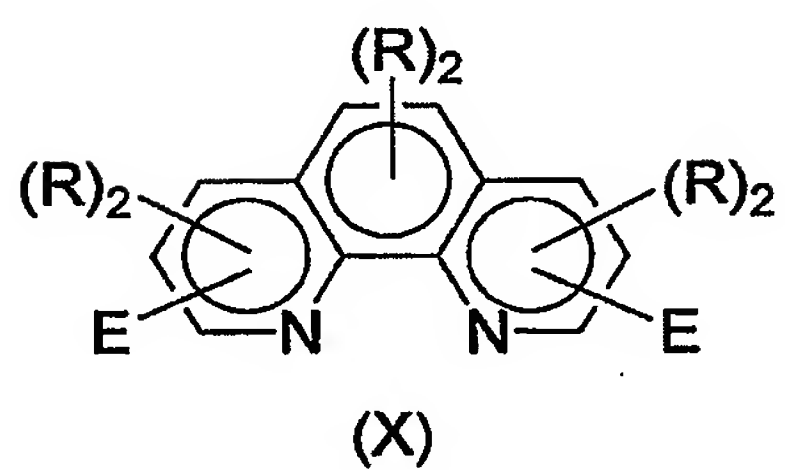
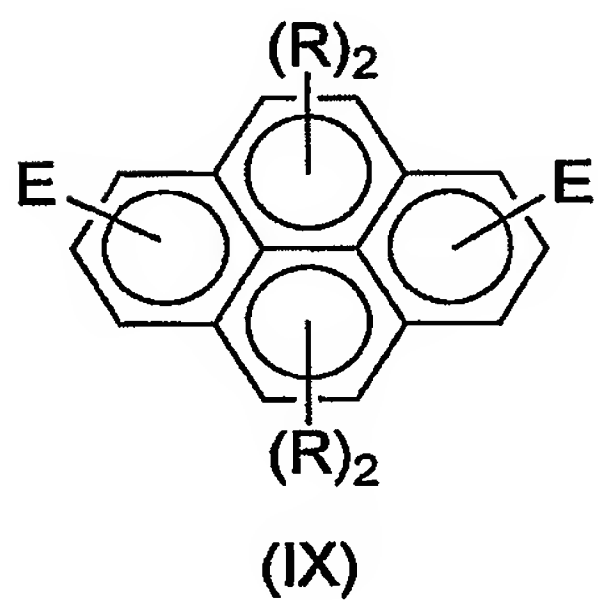
25



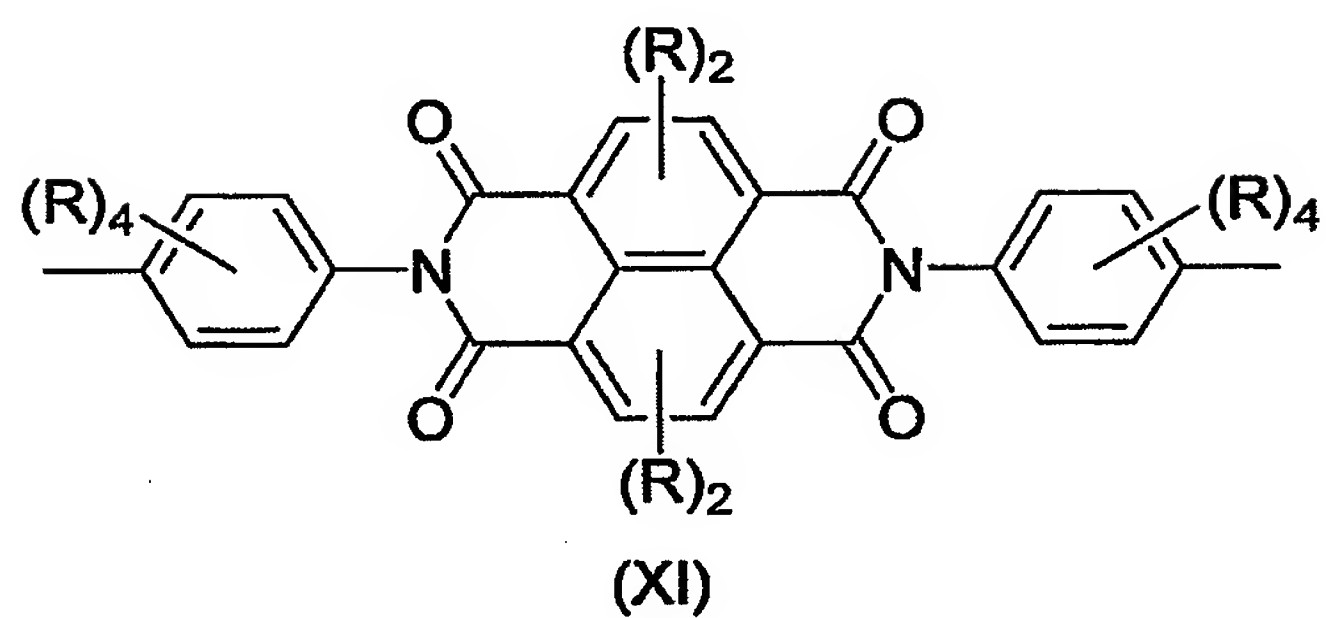
(V)

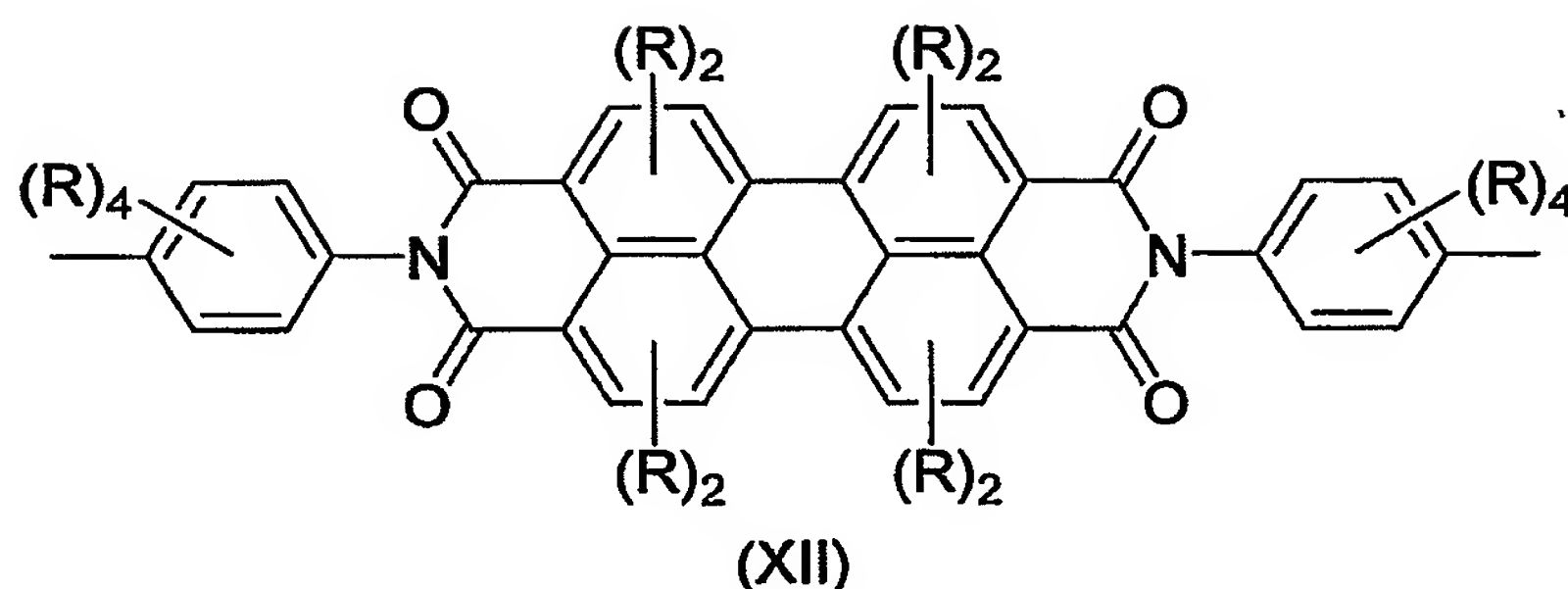


5



10





5 where:

in each of Formulae III through XII:

R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring;

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl

in each of Formulae III, IV, V, VI, VII, VIII, IX and X:

E can be the same or different at each occurrence and is a single bond or a linking group selected from arylene and heteroarylene; in Formula V:

A is independently at each occurrence C or N and  $\gamma$  is 0 or an integer selected from 1 or 2, such that when both A are N, then  $\gamma$  is 0; or when one of A is N and one of A is C, then  $\gamma$  is 1; or when both A are C, then  $\gamma$  is 2;

Q is O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

in Formula VI:

Q<sup>1</sup> is a carbonyl group, O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

$R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

W is H, alkyl or heteroalkyl; or both of W together can represent one single bond;  
in Formula VII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;  
in Formula VIII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10- positions;  
in Formula IX:

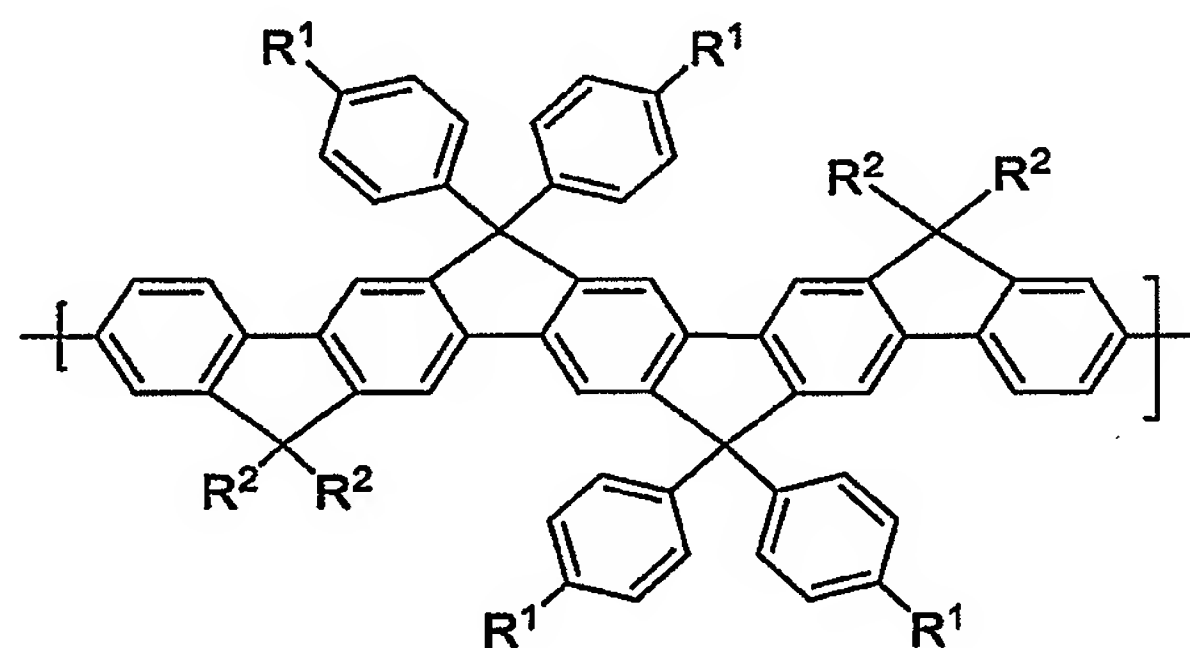
a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8 position; and  
in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

4. A copolymer according to Claim 1, wherein  $R^1$  is a  $C_1$ - $C_{20}$  alkyl.

5. A copolymer according to Claim 1, wherein  $R^2$  is a  $C_1$ - $C_{20}$  alkyl.

6. An electronic device comprising an active layer positioned between two electrical contact layers, wherein the active layer comprises a copolymer comprising at least one monomeric unit having Formula I:



(I)

wherein:

$R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl,

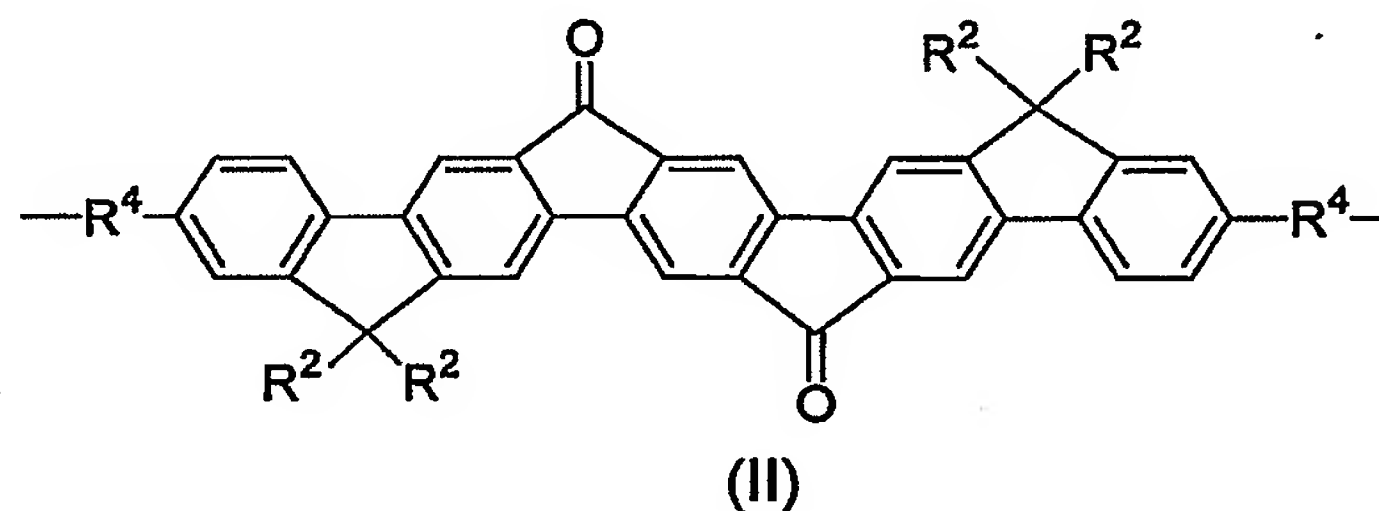
heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

R<sup>2</sup> is the same or different at each occurrence and is selected from, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl.

7. An electronic device according to Claim 6, wherein the copolymer further comprises at least one second monomeric unit comprising an aromatic group.

8. An electronic device according to Claim 7, wherein the second monomeric unit has Formula II:



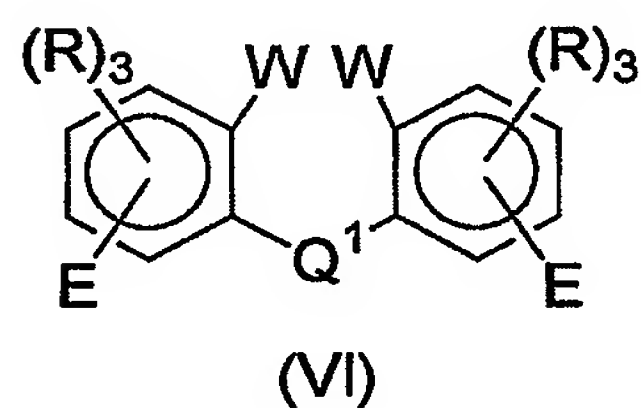
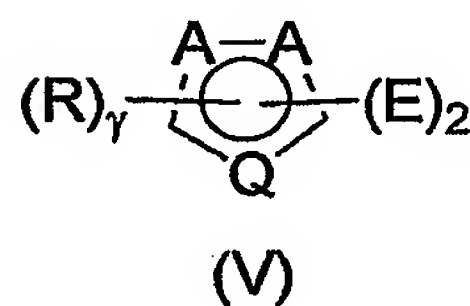
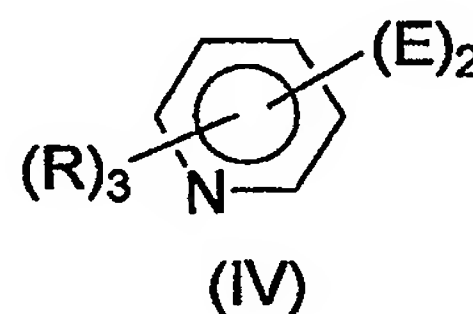
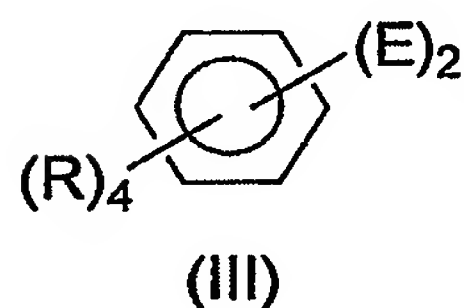
wherein:

R<sup>2</sup> is the same or different at each occurrence and is selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

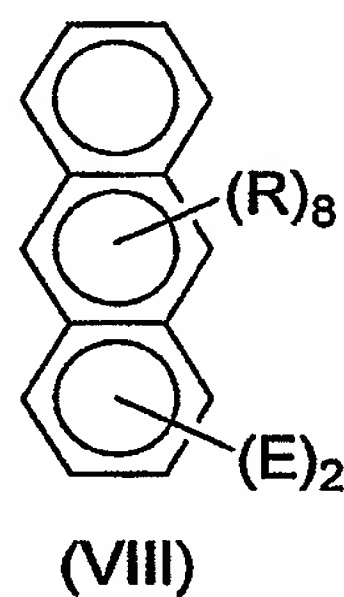
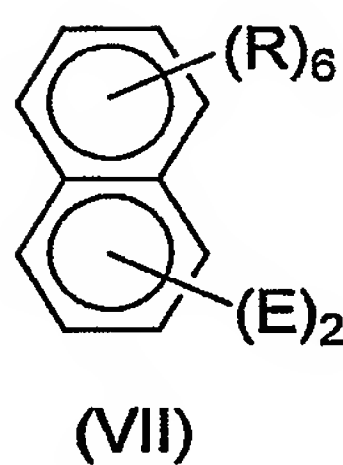


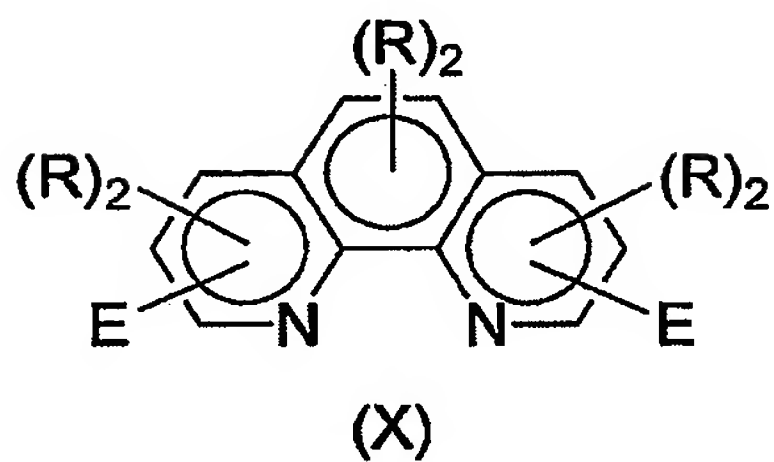
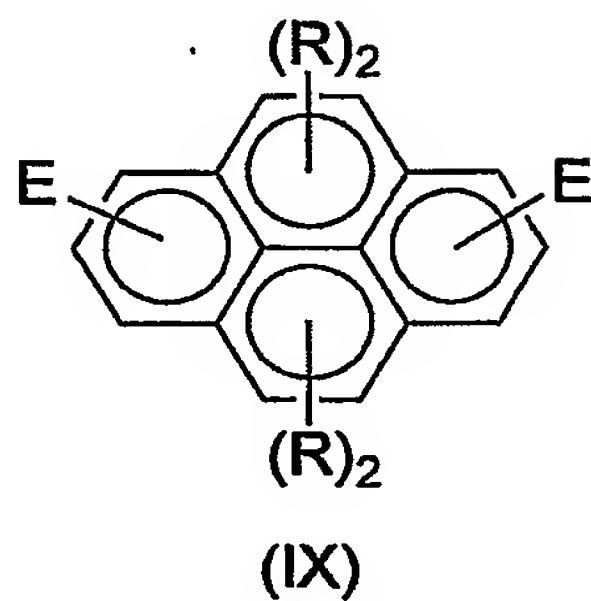
$R^4$  is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

9. An electronic device according to Claim 7, wherein the second monomeric unit has a formula selected from Formula III through Formula XII and combinations thereof,

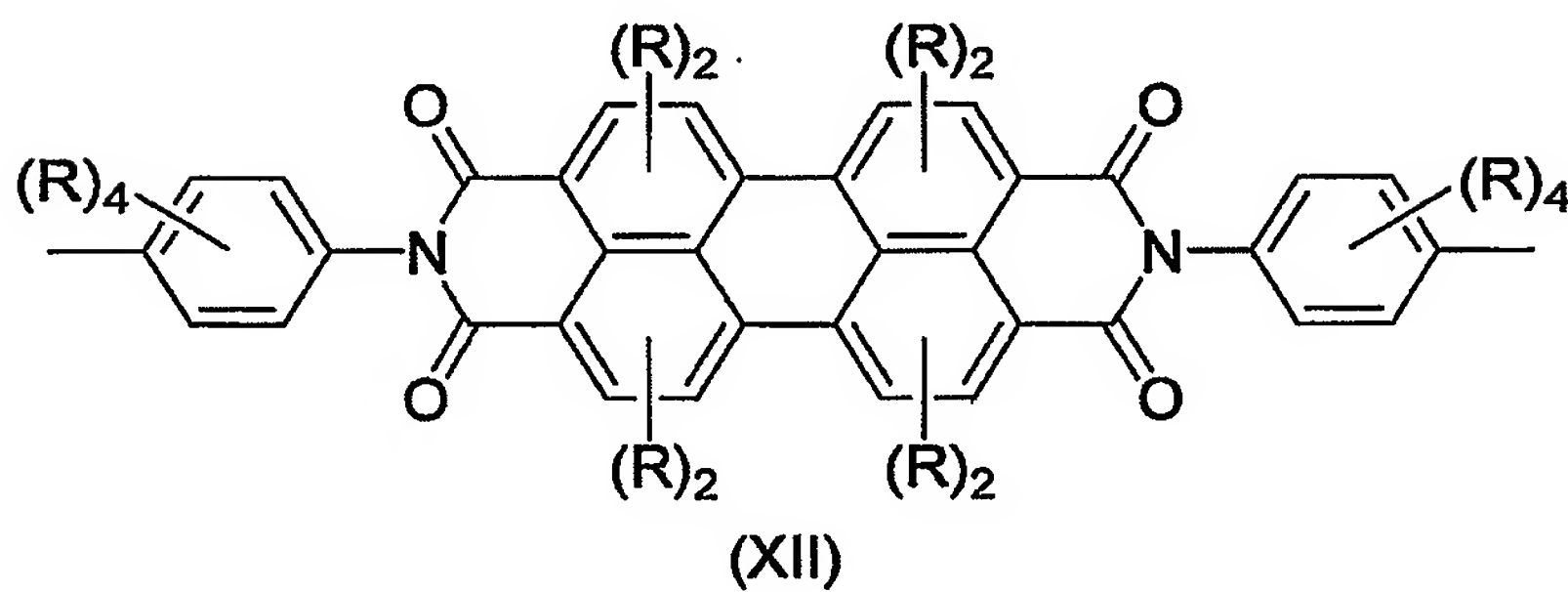
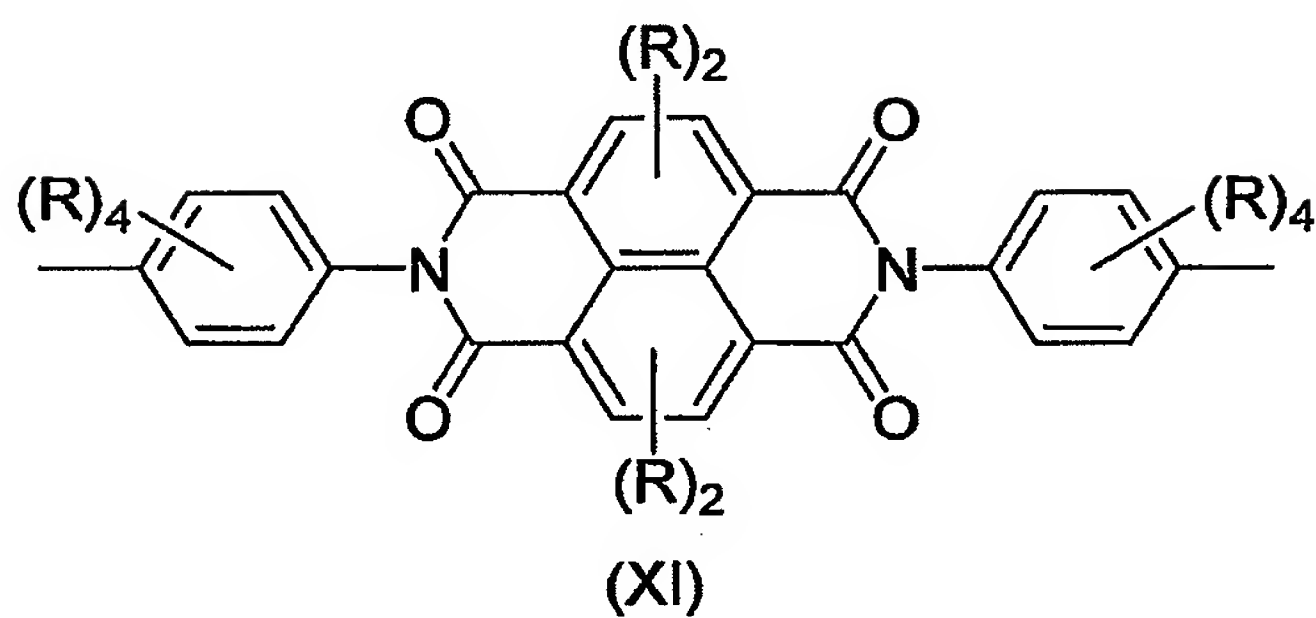


15





5



10

where:

in each of Formulae III through XII:

15

R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub>

oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring;

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl

10 in each of Formulae III, IV, V, VI, VII, VIII, IX and X:

E can be the same or different at each occurrence and is a single bond or a linking group selected from arylene and heteroarylene; in Formula V:

A is independently at each occurrence C or N and  $\gamma$  is 0 or an integer selected from 1 or 2, such that when both A are N, then  $\gamma$  is 0; or when one of A is N and one of A is C, then  $\gamma$  is 1; or when both A are C, then  $\gamma$  is 2;

Q is O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

20 R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

in Formula VI:

Q<sup>1</sup> is a carbonyl group, O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

25 R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

W is H, alkyl or heteroalkyl; or both of W together can represent one single bond;

in Formula VII:

30 the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;

in Formula VIII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10- positions;

in Formula IX:

35 a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8 position; and

in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

10. An electronic device according to Claim 7, wherein the second monomeric unit has a formula



wherein:

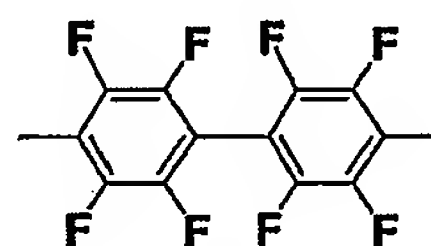
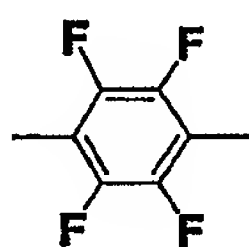
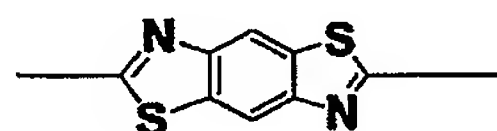
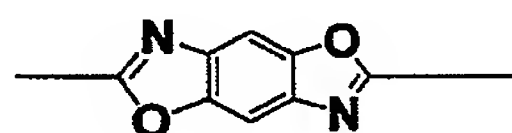
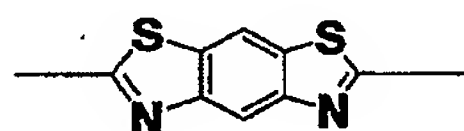
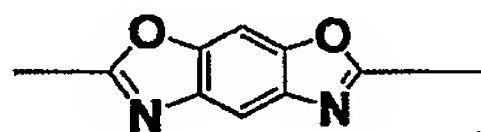
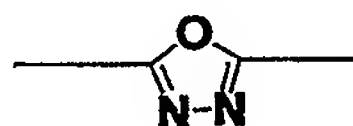
Y is an aromatic group with at least one substituent selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and  $NR^5$ ,  $R^5$  is H or an alkyl; and Z is an electron deficient group.

11. An electronic device according to Claim 10, wherein Y is selected from fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and combinations thereof.

12. An electronic device according to Claim 10, wherein Z is selected from oxazole-type groups, oxadiazole-type groups, thiazole-type groups, fluorinated aromatic groups, and combinations thereof.

13. An electronic device according to Claim 10, wherein Z is selected from:

20



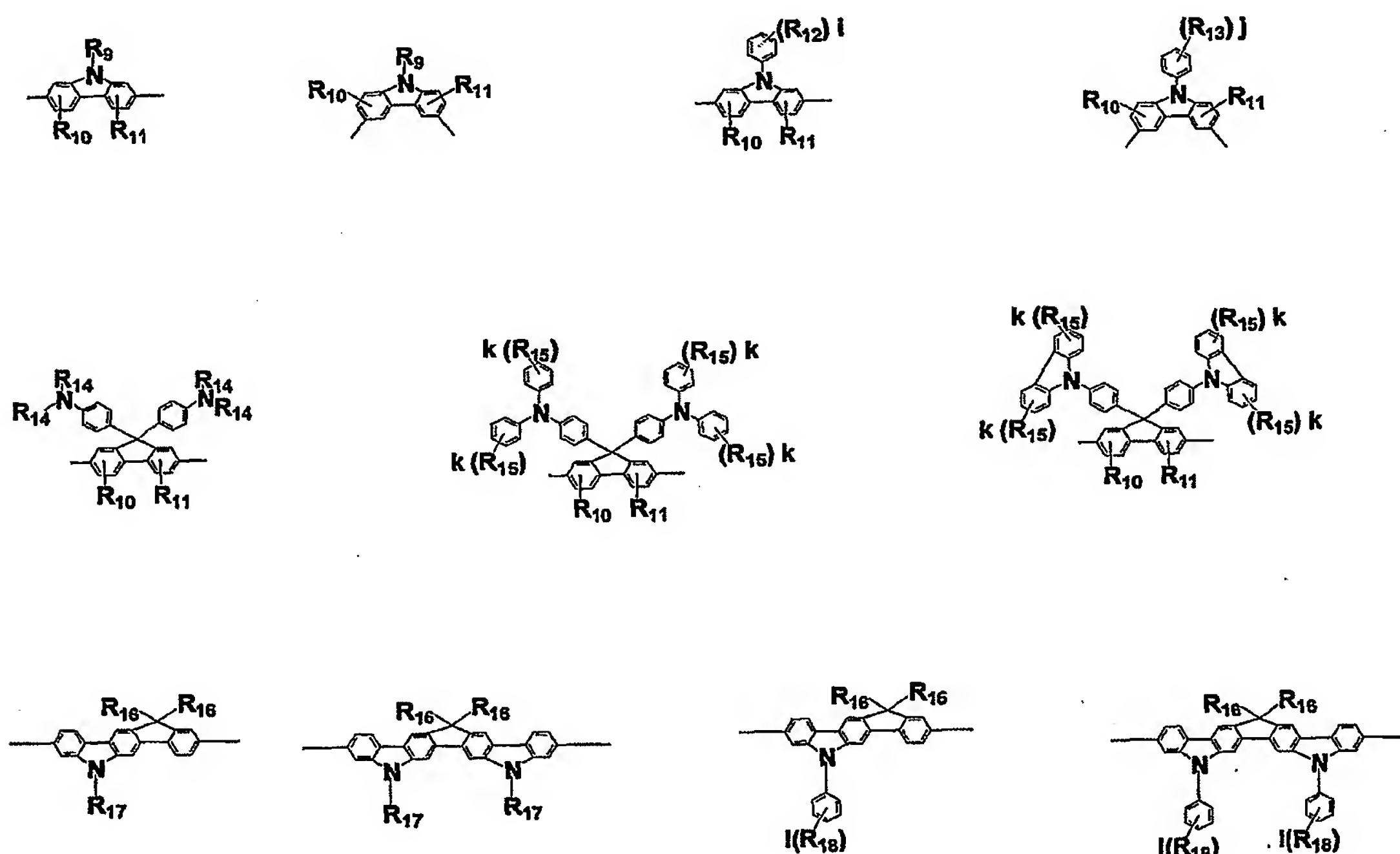
14. An electronic device according to Claim 7, wherein the second monomeric unit has hole transport properties.

15. An electronic device according to Claim 14, wherein the second monomeric unit is selected from carbazoles, triaryl amines, aromatic

groups having carbazole groups, aromatic groups having triarylamine groups, and combinations thereof.

16. An electronic device according to Claim 14, wherein the second monomeric unit is selected from:

5



wherein:

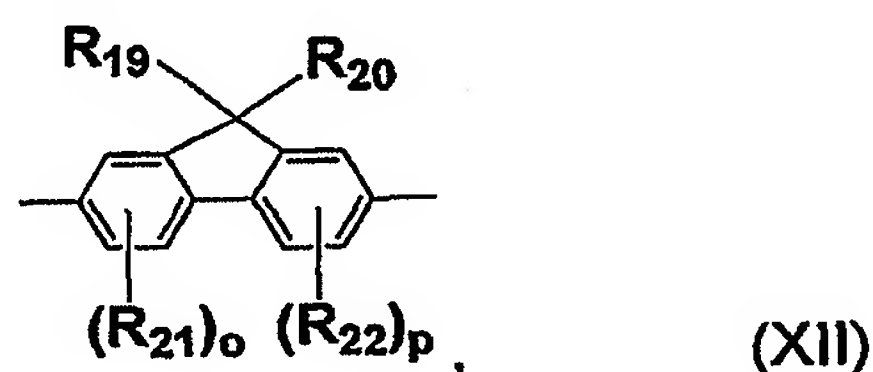
10  $R_9$ - $R_{18}$  are same or different and are selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and  $NR^5$ ,  $R^5$  is H or an alkyl;

$i, j, k, l$  are numbers of substituents on the benzene rings and are same or different and each of  $i, j, k$ , and  $l$  is in a range of 0-3.

15 17. An electronic device according to Claim 7, wherein the second monomeric unit is selected from substituted fluorenes, substituted phenyls, substituted biphenyls, substituted bridged biphenyls, and combinations thereof.

18. An electronic device according to Claim 7, wherein the second monomeric unit has Formula XII:

20





wherein

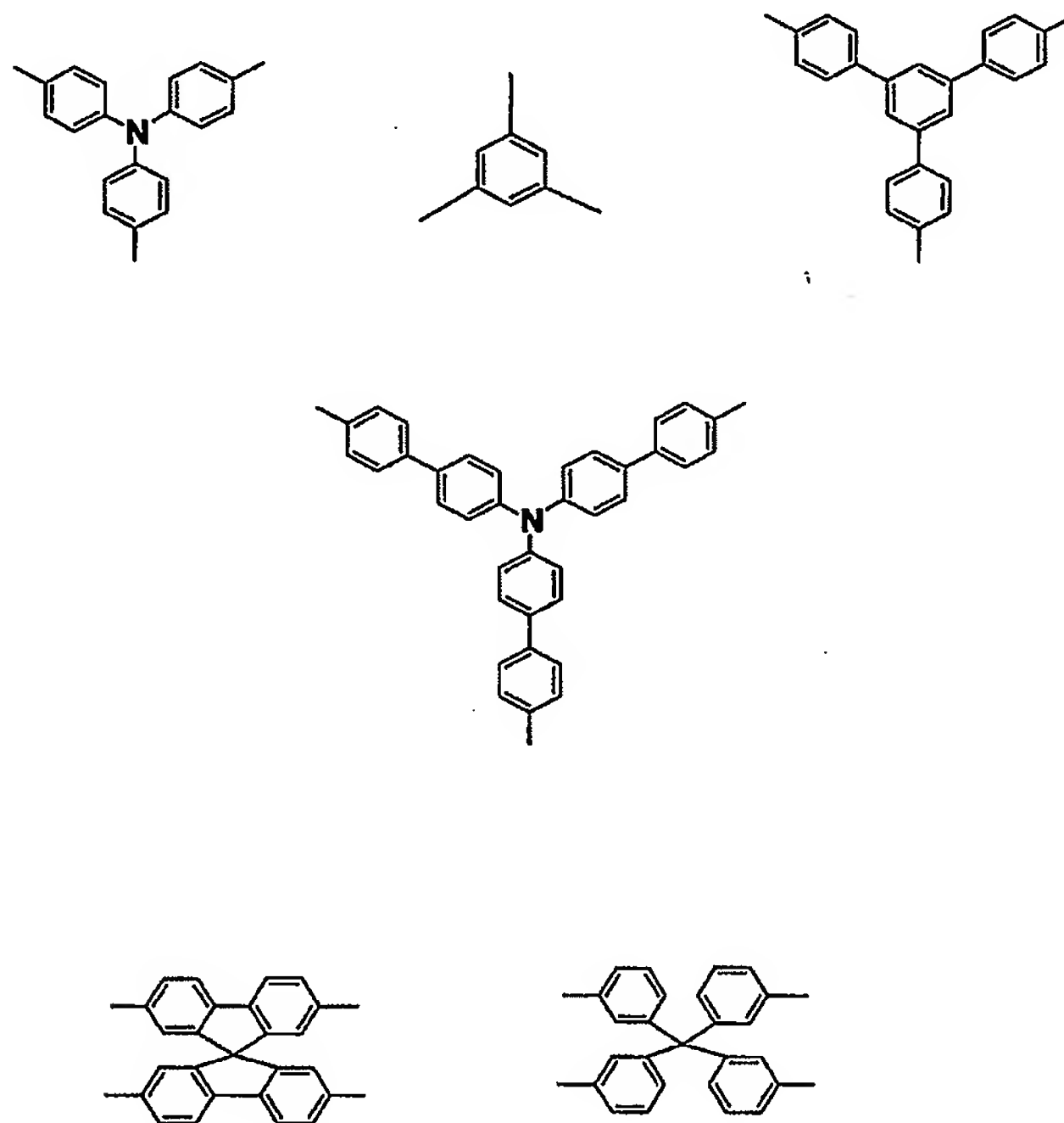
R19-R22 are same or different and are selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and N R<sup>5</sup>,

5 R<sup>5</sup> is H or an alkyl; and

o and p are numbers of substituents on the benzene rings and are same or different and each of o and p is in a range of 0-3.

19. An electronic device according to Claim 7, wherein the second monomeric unit is a branching monomeric unit having more than two linkage sites.

20. An electronic device according to Claim 19, wherein the second monomeric unit is selected from to:



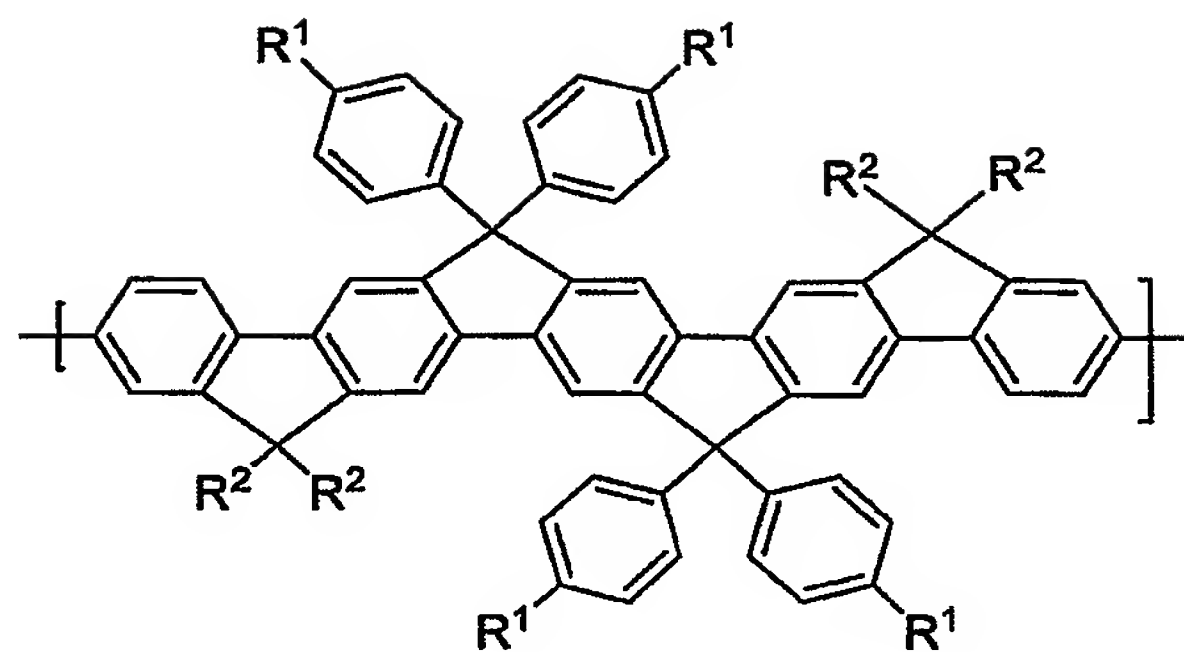
15

20. An electronic device comprising an active layer positioned between two electrical contact layers, wherein the active layer comprises a copolymer having the formula:

20 —(first monomeric unit)<sub>q</sub>—(ED unit)<sub>r</sub>—(SE unit)<sub>s</sub>—(HT unit)<sub>t</sub>—(branching unit)<sub>u</sub>—

wherein:

the first monomeric unit has Formula I:



(I)

wherein:

$R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

$R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

$R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

the ED unit has a formula -Y-Z-Y- wherein:

Y is an aromatic group with at least one substituent selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR<sup>5</sup>,  $R^5$  is H or an alkyl; and

Z is an electron deficient group;

the HT unit is a monomeric unit having hole transport properties;

the SE unit is selected from substituted fluorenes, substituted phenyls, substituted biphenyls, substituted bridged biphenyls, and combinations thereof;

the branching unit is a monomeric unit having more than two  
5 linkage sites;

q is an integer; and

r, s, t, and u are 0 or an integer, with the proviso that at least one of r, s, t, and u is an integer.

10

1/1

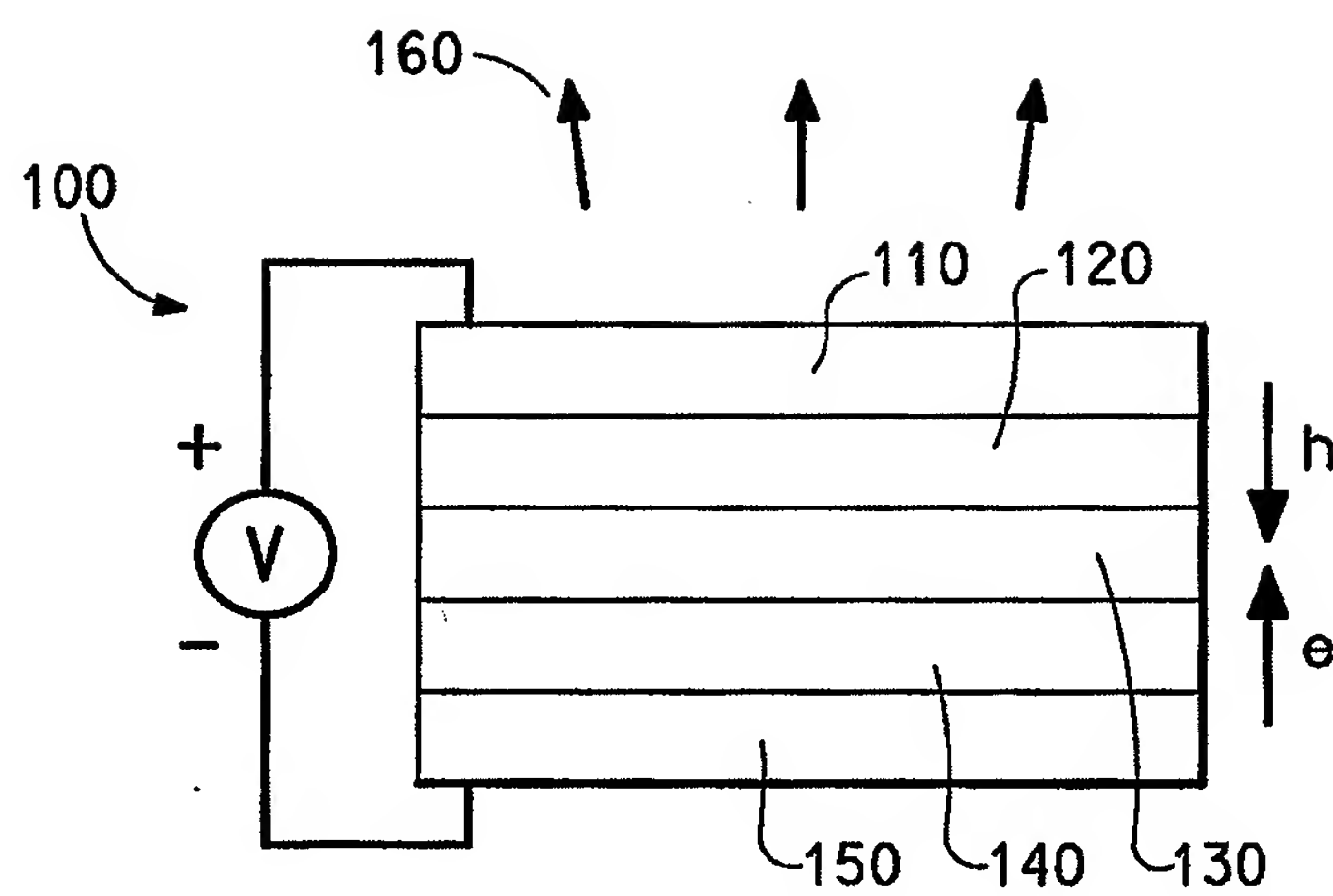


FIG. 1

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/036114

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D3/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/071918 A1 (EMCH DONALDSON J) 13 June 2002 (2002-06-13) paragraphs '0010!, '0028! - '0030!, '0041!, '0043!, '0069!; figures -----	1,5,7-9, 12,13
X	EP 0 426 904 A (POULLOS, MARK; DUNFRIES INVESTMENTS LIMITED) 15 May 1991 (1991-05-15) the whole document -----	1-4,6, 12,13
X	US 6 436 485 B1 (SEDLMEYR MARTIN) 20 August 2002 (2002-08-20) column 5, line 45 - line 55; claim 1 -----	1,7,8, 10,12
X	US 2002/034594 A1 (SHIVELEY JAMES THOMAS) 21 March 2002 (2002-03-21) paragraph '0030! -----	1,2,4,12
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 March 2005

Date of mailing of the international search report

18/03/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Brothier, J-A



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/036114

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/148039 A1 (BLUM RAINER ET AL) 7 August 2003 (2003-08-07) paragraphs '0103!, '0153!, '0154! -----	1,2,7,8, 12
E	WO 2004/110652 A (ALLIANCE SURFACE FINISHING INC; LANGLOIS, ROBERT, W) 23 December 2004 (2004-12-23) the whole document -----	1,2,4, 12,13
A	US 5 060 594 A (TOMIOKA ET AL) 29 October 1991 (1991-10-29) column 5, line 6 - column 6, line 5 -----	1-12
A	WO 02/066220 A (EXFO PHOTONIC SOLUTIONS INC; MARTIN, STEVE) 29 August 2002 (2002-08-29) paragraphs '0032!, '0034! -----	1

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/036114

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2002071918	A1	13-06-2002	US 2002015801 A1	07-02-2002
			US 6221441 B1	24-04-2001
			US 2003104133 A1	05-06-2003
			US 2004043156 A1	04-03-2004
			AT 238106 T	15-05-2003
			AU 4849600 A	18-12-2000
			BR 0011605 A	16-04-2002
			CA 2374135 A1	07-12-2000
			DE 60002343 D1	28-05-2003
			DE 60002343 T2	04-03-2004
			EP 1204484 A2	15-05-2002
			ES 2197096 T3	01-01-2004
			PT 1204484 T	29-08-2003
			WO 0072978 A2	07-12-2000
EP 0426904	A	15-05-1991	EP 0426904 A1	15-05-1991
			AT 122587 T	15-06-1995
			DE 68922731 D1	22-06-1995
			DE 68922731 T2	21-12-1995
US 6436485	B1	20-08-2002	DE 19831781 A1	27-01-2000
			AU 3035299 A	11-10-1999
			BR 9908843 A	21-11-2000
			CA 2324097 A1	23-09-1999
			CN 1293598 A	02-05-2001
			DE 59902341 D1	19-09-2002
			WO 9947276 A1	23-09-1999
			EP 1062053 A1	27-12-2000
			ES 2182500 T3	01-03-2003
			JP 2002506725 T	05-03-2002
US 2002034594	A1	21-03-2002	NONE	
US 2003148039	A1	07-08-2003	DE 10009822 C1	06-12-2001
			WO 0164794 A2	07-09-2001
			EP 1259571 A2	27-11-2002
WO 2004110652	A	23-12-2004	CA 2432836 A1	13-12-2004
			WO 2004110652 A1	23-12-2004
			US 2004253373 A1	16-12-2004
US 5060594	A	29-10-1991	JP 1921127 C	07-04-1995
			JP 3026366 A	04-02-1991
			JP 6047094 B	22-06-1994
			JP 2670860 B2	29-10-1997
			JP 3038275 A	19-02-1991
			JP 3135474 A	10-06-1991
			CA 2012161 A1	12-12-1990
			GB 2233257 A ,B	09-01-1991
WO 02066220	A	29-08-2002	US 2002114879 A1	22-08-2002
			WO 02066220 A1	29-08-2002
			CA 2353184 A1	21-08-2002
			CA 2372523 A1	21-08-2002
			US 2002114896 A1	22-08-2002

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
12 May 2005 (12.05.2005)

PCT

(10) International Publication Number  
**WO 2005/042176 A3**

(51) International Patent Classification:

**C09K 11/06** (2006.01)      **C08G 61/02** (2006.01)  
**H05B 33/14** (2006.01)      **C08G 61/10** (2006.01)  
**H01L 51/30** (2006.01)      **C08G 61/12** (2006.01)

(21) International Application Number:

PCT/US2004/036116

(22) International Filing Date: 28 October 2004 (28.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

10/696,057      29 October 2003 (29.10.2003)      US

(71) Applicant (for all designated States except US): **E.I. DUPONT DE NEMOURS AND COMPANY** [US/US];  
1007 MARKET STREET, WILMINGTON, Delaware  
19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **UCKERT, Frank, P.**  
[DE/US]; 545 Willow Lane, Buellton, California 93427  
(US).

(74) Agent: **CAPRIA, Mary, Ann; E. I. DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER**, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:  
9 March 2006

(15) Information about Correction:

Previous Correction:

see PCT Gazette No. 01/2006 of 5 January 2006, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **LIGHT-EMITTING COPOLYMERS AND ELECTRONIC DEVICES USING SUCH COPOLYMERS**

(57) Abstract: The invention provides novel pentaphenylene copolymers which are useful in electronic devices.

WO 2005/042176 A3

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/036116

## A. CLASSIFICATION OF SUBJECT MATTER

C09K11/06 H05B33/14 H01L51/30 C08G61/02 C08G61/10  
C08G61/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K H05B H01L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/092723 A (CAMBRIDGE DISPLAY TECHNOLOGY LIMITED; TOWNS, CARL, ROBERT; O'DELL, RIC) 21 November 2002 (2002-11-21) the whole document	1-21
A	SCHERF, U.: "Ladder-type materials" JOURNAL OF MATERIALS CHEMISTRY, vol. 9, 1999, pages 1853-1864, XP002353303 cited in the application the whole document	1-21

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

10 November 2005

Date of mailing of the international search report

22/11/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Meiners, C

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/036116

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 02092723	A	21-11-2002	AT 292662 T 15-04-2005
			AT 273363 T 15-08-2004
			CN 1513044 A 14-07-2004
			DE 60200951 D1 16-09-2004
			DE 60200951 T2 27-01-2005
			DE 60203610 D1 12-05-2005
			DE 60203610 T2 15-09-2005
			EP 1385918 A1 04-02-2004
			EP 1385919 A1 04-02-2004
			WO 02092724 A1 21-11-2002
			HK 1062832 A1 24-06-2005
			JP 2004527628 T 09-09-2004
			JP 2004532325 T 21-10-2004



CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
12 May 2005 (12.05.2005)

PCT

(10) International Publication Number  
WO 2005/042176 A2

(51) International Patent Classification<sup>7</sup>: Not classified

(21) International Application Number:  
PCT/US2004/036116

(22) International Filing Date: 28 October 2004 (28.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/696,057 29 October 2003 (29.10.2003) US

(71) Applicant (for all designated States except US): E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 MARKET STREET, WILMINGTON, Delaware 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): UCKERT, Frank, P. [DE/US]; 545 Willow Lane, Buellton, California 93427 (US).

(74) Agent: CAPRIA, Mary, Ann; E. I. DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

(48) Date of publication of this corrected version:  
5 January 2006

(15) Information about Correction:  
see PCT Gazette No. 01/2006 of 5 January 2006, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LIGHT-EMITTING COPOLYMERS AND ELECTRONIC DEVICES USING SUCH COPOLYMERS

(57) Abstract: The invention provides novel pentaphenylene copolymers which are useful in electronic devices.

WO 2005/042176 A2

TITLELIGHT-EMITTING COPOLYMERS AND ELECTRONIC DEVICES  
USING SUCH COPOLYMERSTHE INVENTION

5           The invention relates generally to pentaphenylene copolymers, and their use in electronic devices.

BACKGROUND INFORMATION

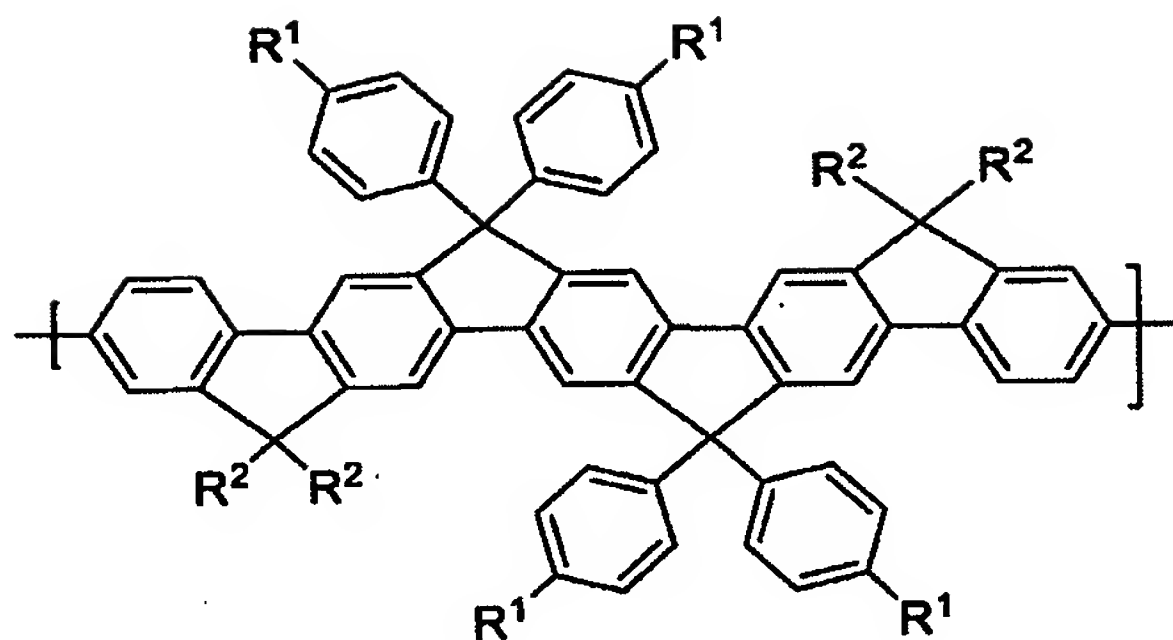
Organic electronic devices are present in many different kinds of electronic equipment. In such devices, an active layer is sandwiched  
10   between two electrical contact layers. At least one of the electrical contact layers is light-transmitting so that light can pass through the electrical contact layer. One type of electronic device is an organic light emitting diode (OLED), which holds promise for display applications due to its high power conversion efficiency and low processing costs. Such displays are  
15   especially promising for battery-powered, portable electronic devices, including cell-phones, personal digital assistants, handheld personal computers, and DVD players. These applications call for displays with high information content, full color, and fast video rate response time in addition to low power consumption.

20           OLED's typically contain electroluminescent (EL) layers arranged between an anode and a cathode. Types of electroluminescent materials which have been used in OLED's include fluorescent dyes, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. Several classes of luminescent polymers have also been  
25   disclosed. These include, for example, poly(1,4-phenylene vinylene) and derivatives; polythiophenes, especially, poly(3-alkylthiophenes); and poly(p-phenylenes). Alkyl and dialkyl derivatives of polyfluorene have also been disclosed.

There is a continuing need for active compounds having the necessary  
30   efficiency and color. In particular, blue-emitting polymers are desirable.

SUMMARY OF THE INVENTION

The invention provides a copolymer comprising a first monomeric unit having Formula I below:



(I)

wherein:

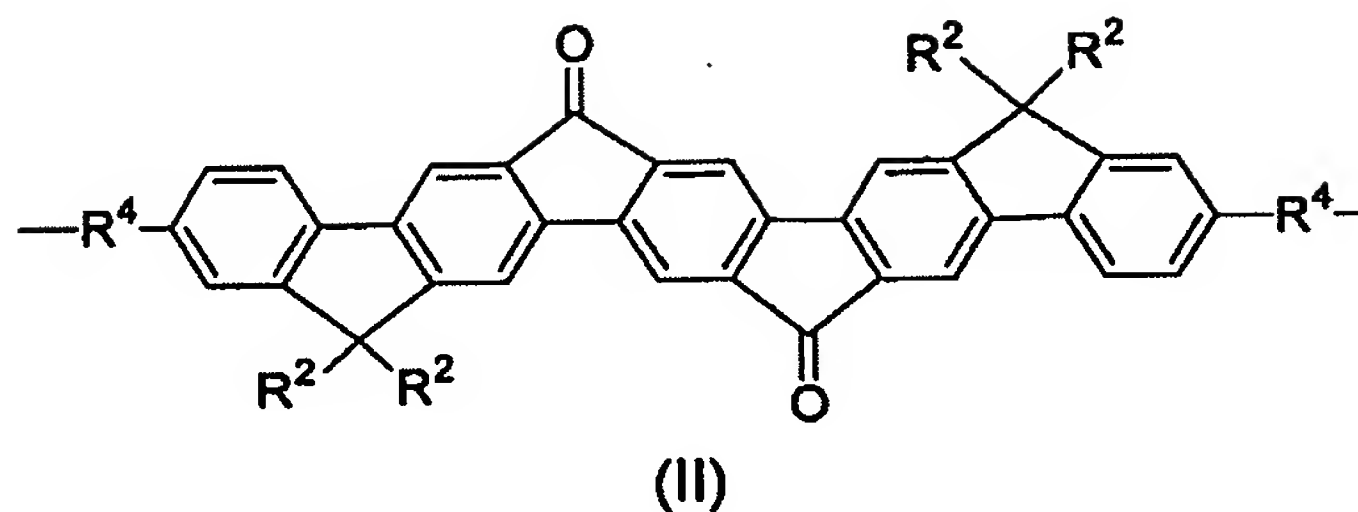
5  $R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

15  $R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

25  $R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

and at least one second monomeric unit comprising an aromatic group.

30 In one embodiment, the invention relates to a copolymer comprising the first monomeric unit and a second monomeric unit having Formula II below:



5 wherein:

$R^2$  is as defined above, and

$R^4$  is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

10 In one embodiment, the invention relates to an electronic device having an active layer comprising at least one of the above copolymers.

As used herein, the term "aromatic group" is intended to mean an organic group comprising at least one unsaturated cyclic group having delocalized pi electrons. The term is intended to encompass both aromatic hydrocarbon groups having only carbon and hydrogen atoms, and heteroaromatic groups wherein one or more of the carbon atoms within the cyclic group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "alkyl" refers to a monovalent straight or branched chain hydrocarbon group. The term "alkylene" refers to an alkyl group having two points of attachment.

As used herein, "alkoxy" refers to the moiety -O-alkyl-, wherein alkyl is as defined above.

As used herein, "oxyalkyl" refers to alkyl moieties in which at least one -CH<sub>2</sub>- unit of the alkyl moiety has been replaced by an oxygen atom.

As used herein, "alkenyl" refers to straight or branched chain hydrocarbyl groups having one or more carbon-carbon double bonds.

As used herein, "oxyalkenyl" refers to alkenyl moieties in which at least one -CH<sub>2</sub>- unit of the alkenyl moiety has been replaced by an oxygen atom.

As used herein, "alkynyl" refers to straight or branched chain hydrocarbyl groups having one or more carbon-carbon triple bonds.

As used herein, "oxyalkynyl" refers to alkynyl moieties in which at least one -CH<sub>2</sub>- unit of the alkenyl moiety has been replaced by an oxygen atom.

As used herein, "fluorinated" means that at least one hydrogen atom of the moiety has been replaced with a fluorine atom.

As used herein, the terms "heteroalkyl", "heteroalkenyl", and "heteroalkynyl" are intended to mean an alkyl group, an alkenyl group, and an alkynyl group, respectively, wherein one or more of the carbon atoms within the group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "aryl" is intended to mean a group derived from an aromatic hydrocarbon which may be unsubstituted or substituted. The term "arylene" refers to an aryl group having two points of attachment. The term "heteroaryl" is intended to mean an aryl group, wherein one or more of the carbon atoms within the aryl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "active material" is intended to mean a material which is electrically active or photoactive. Electrically active materials include conductive and semiconductive materials. The term "photoactive" refers to any material that exhibits electroluminescence, photoluminescence, and/or photosensitivity.

As used herein, the term "blue," is intended to mean any color that appears bluish to the naked human eye, including light of wavelengths ranging from 400 nm to 540 nm.

As used herein, the term "emission maximum" is intended to mean the wavelength, in nanometers, at which the maximum intensity of electroluminescence is obtained. Electroluminescence is generally measured in a diode structure, in which the material to be tested is sandwiched between two electrical contact layers and a voltage is applied. The light intensity and wavelength can be measured, for example, by a photodiode and a spectrograph, respectively.

As used herein, the term "monomeric unit" is intended to mean a repeating unit within a polymeric structure.

As used herein, the term "degree of polymerization" is intended to mean the total number of monomeric units in a polymer.

The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1-18 (CRC Handbook of Chemistry and Physics, 81<sup>st</sup> Edition, 2000).



As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of the "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In the formulae, all letters not otherwise defined, are used to designate conventional atomic symbols. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated by way of example and not limitation in the accompanying figures.

FIG. 1 includes an illustration of a cross-sectional view of an electronic device that includes a polymer in accordance with an embodiment of the present invention.

Skilled artisans appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures



may be exaggerated relative to other elements to help to improve understanding of embodiments of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The copolymer of the invention has a first monomeric unit having  
5 Formula I above which comprises a planar ladder-type pentaphenylene unit. This structure is intermediate between the monomeric units in fully ladder-type poly(p-phenylene) polymers ("LPPP") (reviewed by Scherf, *J. Mater. Chem.*, 1999, 9, 1853) and fluorene monomeric units (recent reviews are Neher, *Macromol. Rapid Commun.*, 2001, 22, 1365 and  
10 Scherf and List, *Adv. Mater.*, 2002, 14, 477).

In the copolymers of the invention the rigidity of the first monomeric unit structure produces a small Stokes shift and high fluorescence efficiency. The aryl substituents improve the stability of the polymer against oxidation as previously shown in polyfluorenes (Müllen et al,  
15 *JACS*, 2001, 123, 946; *Adv. Mater.*, 2002, 13, 809), while the avoidance of polymer analogous reaction steps avoids defects due to incomplete ring closure as is possible in LPPP.

The copolymers of the invention may exhibit blue electroluminescence. In one embodiment, the copolymer has an emission  
20 maximum less than 450 nm.

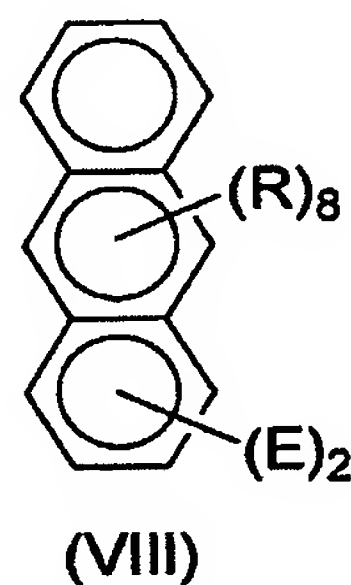
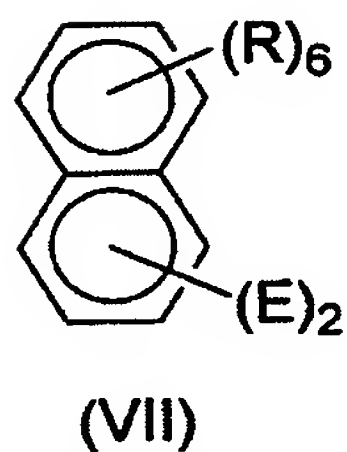
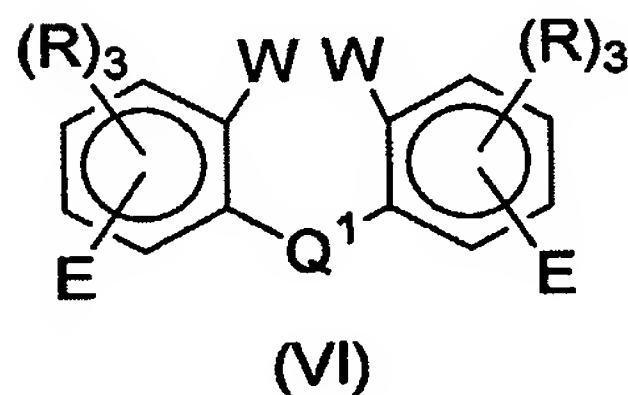
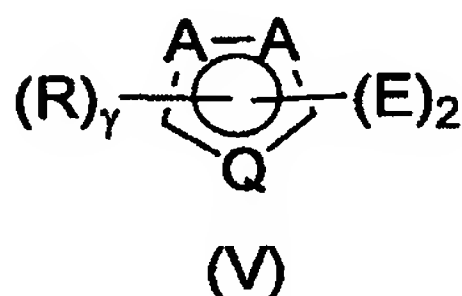
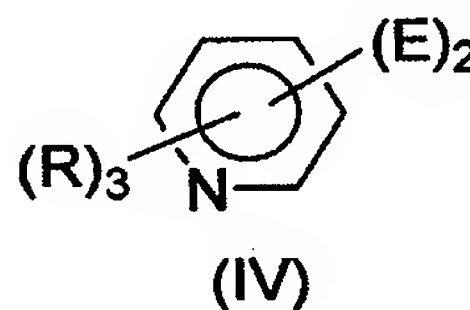
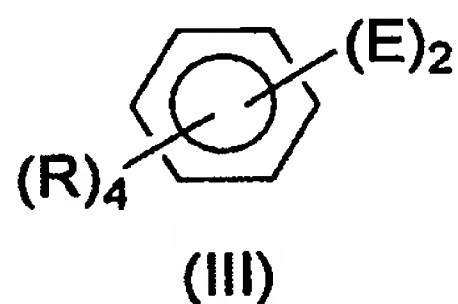
In one embodiment of Formula I, R<sup>1</sup> is selected from C<sub>1-20</sub> alkyls. In one embodiment, R<sup>1</sup> is selected from C<sub>1-10</sub> alkyls. In one embodiment all R<sup>1</sup> groups are the same. In one embodiment R<sup>2</sup> is selected from C<sub>1-20</sub> alkyls. In one embodiment R<sup>2</sup> is selected from C<sub>1-10</sub> alkyls. In one  
25 embodiment all R<sup>2</sup> groups are the same.

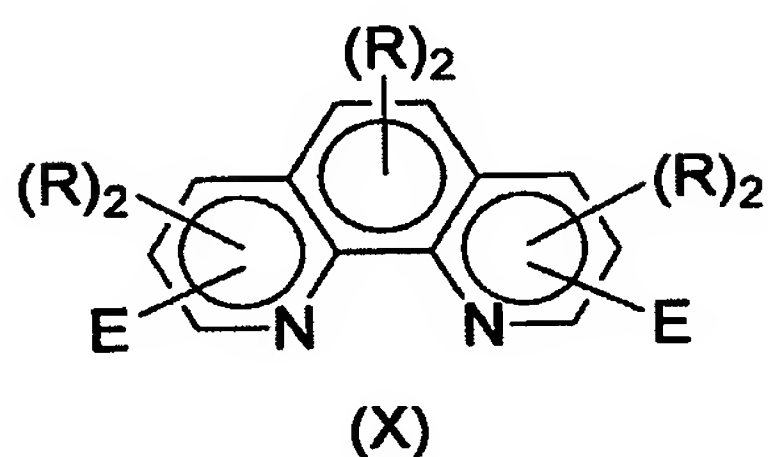
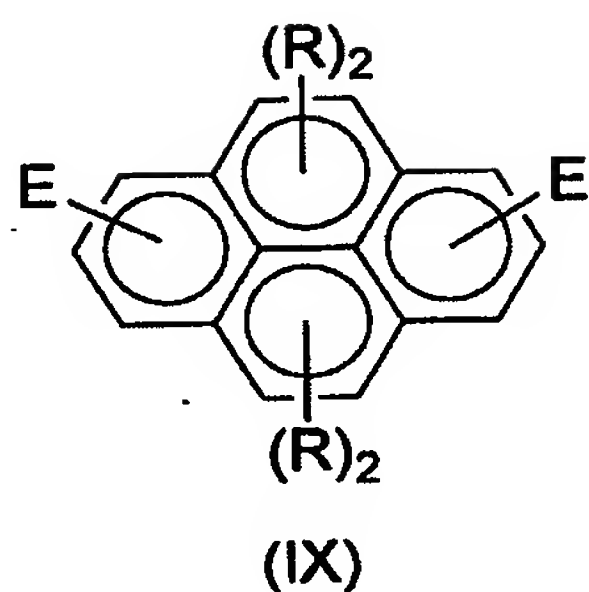
In the copolymers of the invention, there is at least one second monomeric unit comprising an aromatic group. Such monomeric units can be derived from mono- and polycyclic aromatic hydrocarbons and heteroaromatics. Examples of suitable aromatic groups include, but are  
30 not limited to, fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and the like, including mono- and poly-hetero analogs, and combinations thereof. The aromatic group can be substituted at one or more positions.

In one embodiment of the invention, the second monomeric unit  
35 comprises Formula II. This monomeric unit has an electron accepting property. In one embodiment of Formula II, R<sup>4</sup> is selected from and single bond and a phenylene. In one embodiment all R<sup>4</sup> groups are the same. In one embodiment R<sup>2</sup> is selected from C<sub>1-20</sub> alkyls. In one embodiment R<sup>2</sup>

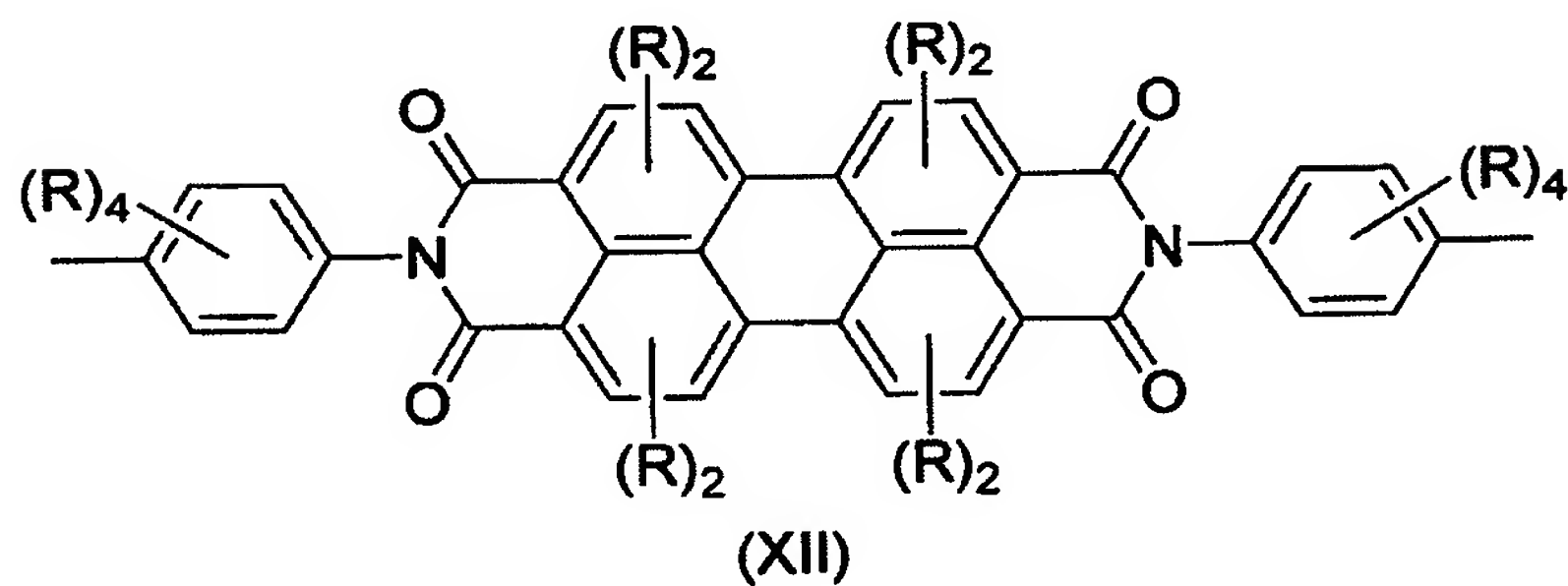
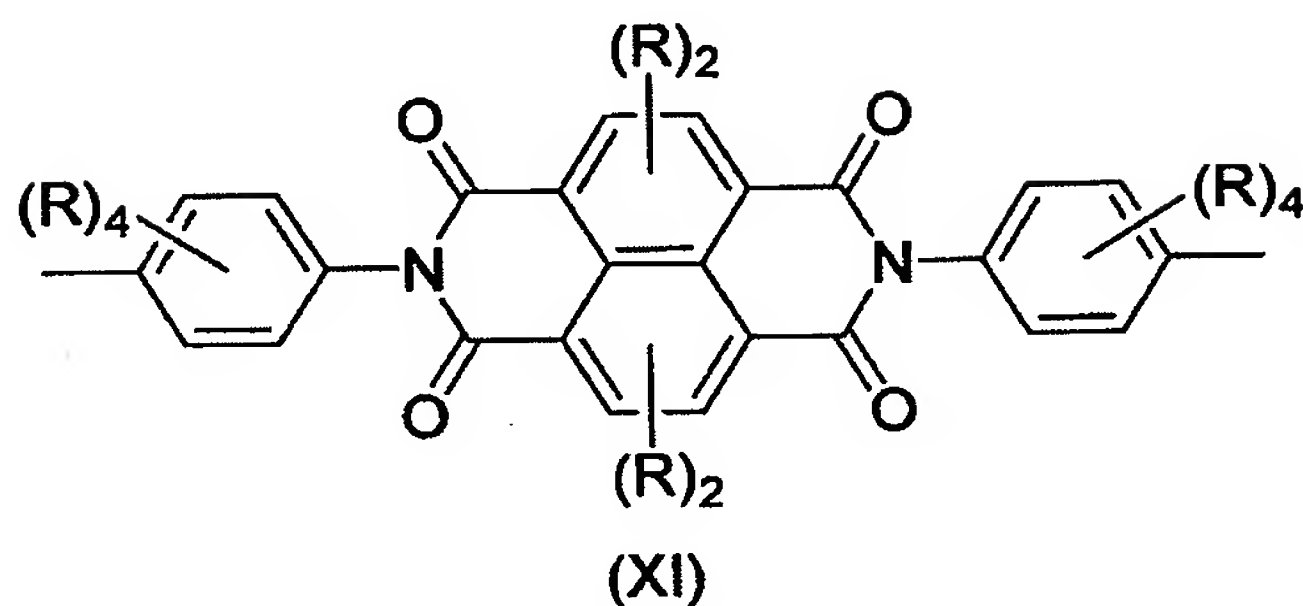
is selected from C<sub>1-10</sub> alkyls. In one embodiment all R<sup>2</sup> groups are the same.

In one embodiment of the invention, the at least one second monomeric unit is selected from (i) aromatic groups having Formula III below; (ii) 6-membered-ring heteroaromatic groups having Formula IV below; (iii) 5-membered-ring heteroaromatic groups having Formula V below; (iv) aromatic groups having Formula VI below; (v) fused ring aromatic groups having Formula VII through Formula XII below; and (vi) combinations thereof,





5



10

where:

in each of Formulae III through XII:

15

R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub>

5 fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring;

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl

10 in each of Formulae III, IV, V, VI, VII, VIII, IX and X:

E can be the same or different at each occurrence and is a single bond or a linking group selected from arylene and heteroarylene;

in Formula V:

15 A is independently at each occurrence C or N and  $\gamma$  is 0 or an integer selected from 1 or 2, such that when both A are N, then  $\gamma$  is 0; or when one of A is N and one of A is C, then  $\gamma$  is 1; or when both A are C, then  $\gamma$  is 2;

Q is O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

20 R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

in Formula VI:

Q<sup>1</sup> is a carbonyl group, O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

25 R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

W is H, alkyl or heteroalkyl; or both of W together can represent one single bond;

30 in Formula VII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;

in Formula VIII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10- positions;

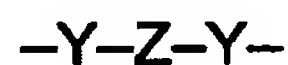
in Formula IX:

35 a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8 position; and

in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

In one embodiment of the invention, the second monomeric unit  
5 comprises an electron deficient group ("ED unit") and has a formula



wherein:

10 Y is an aromatic group with at least one substituent selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR<sup>5</sup>,

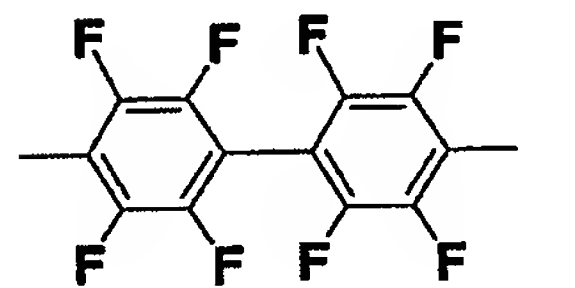
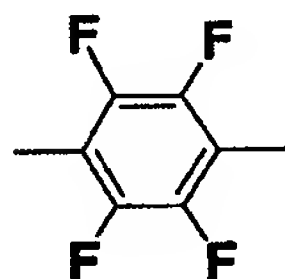
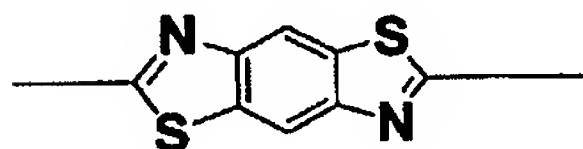
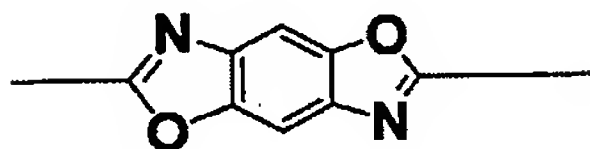
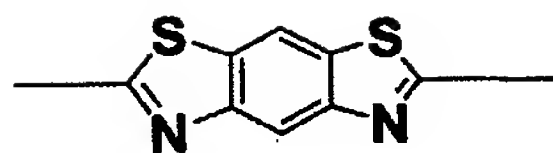
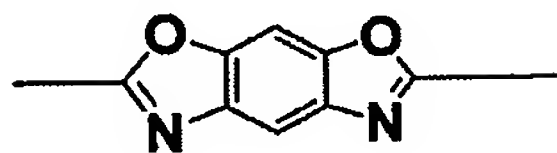
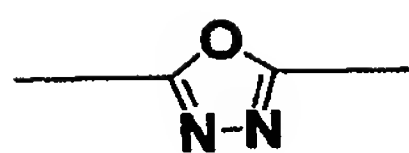
R<sup>5</sup> is H or an alkyl; and

Z is an electron deficient group.

15 Examples of suitable aromatic groups for Y include mono- and polycyclic aromatic hydrocarbons, such as fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and the like. The aromatic group can be substituted at one or more positions, preferably two positions. In one embodiment, the substituents are alkyl  
20 groups having from 1 to 20 carbon atoms. In one embodiment the Y groups are fluorenes with two alkyl groups in the 9-position.

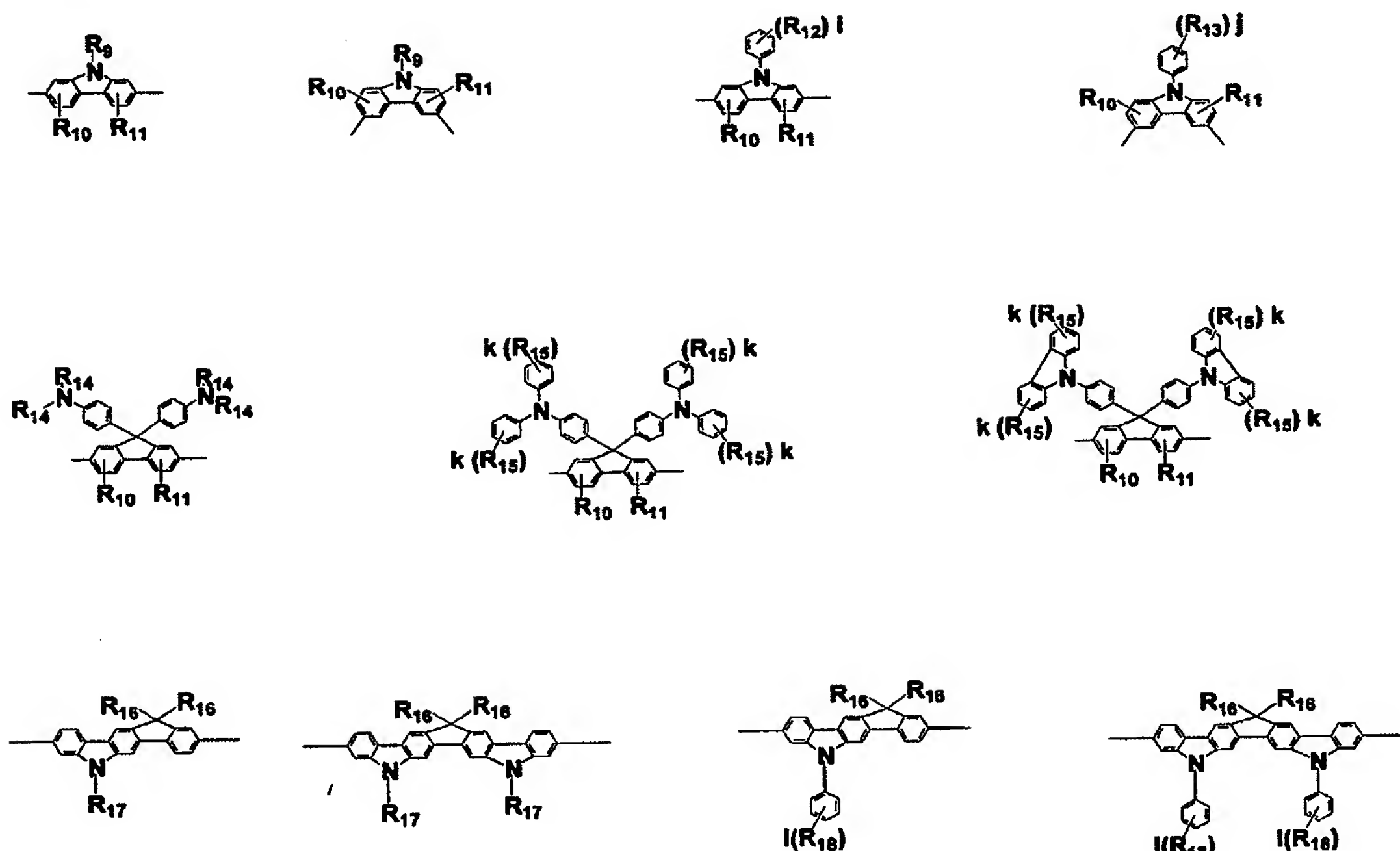
Examples of suitable electron deficient groups for Z include heteroaromatic groups having heteroatoms selected from O, N, and S, and fluorinated aromatic groups. In one embodiment, Z is selected from  
25 oxazole-type, oxadiazole-type, thiazole-type, and fluorinated aromatic groups, such as phenyls and biphenyls.

In one embodiment, the Z group is selected from:



In one embodiment of the invention, the second monomeric unit is one having hole transport properties ("HT unit"). In general, the HT monomeric unit has an electron rich group. Examples of suitable HT monomeric units include, but are not limited to, carbazoles, triarylamine, and aromatic groups having carbazole or triarylamine groups. Of particular interest as hole-transport monomers are the N-aryl carbazoles with alkyl substituents as they have better solubility and better processibility compared to other hole-transport monomers. Specific examples include:



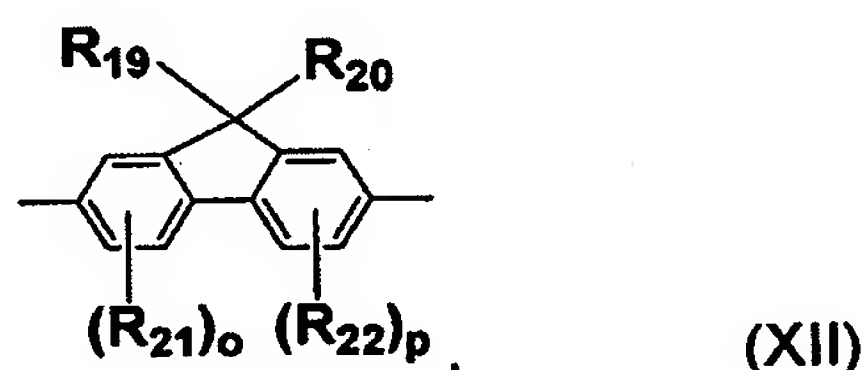


wherein:

$R_9$ - $R_{18}$  are same or different and are selected from alkyl,  
heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and  $NR^5$ ,  
 $R^5$  is H or an alkyl;

$i, j, k, l$  are numbers of substituents on the benzene rings and are  
same or different and each of  $i, j, k$ , and  $l$  is in a range of 0-3.

In one embodiment of the invention, the second monomeric unit is  
one which enhances the solubility of the resulting polymer ("SE unit").  
Examples of suitable SE monomeric units include, but are not limited to,  
substituted fluorenes, substituted phenyls, substituted biphenyls, and  
substituted bridged biphenyls. In one embodiment, the SE monomeric unit  
has Formula XII below:

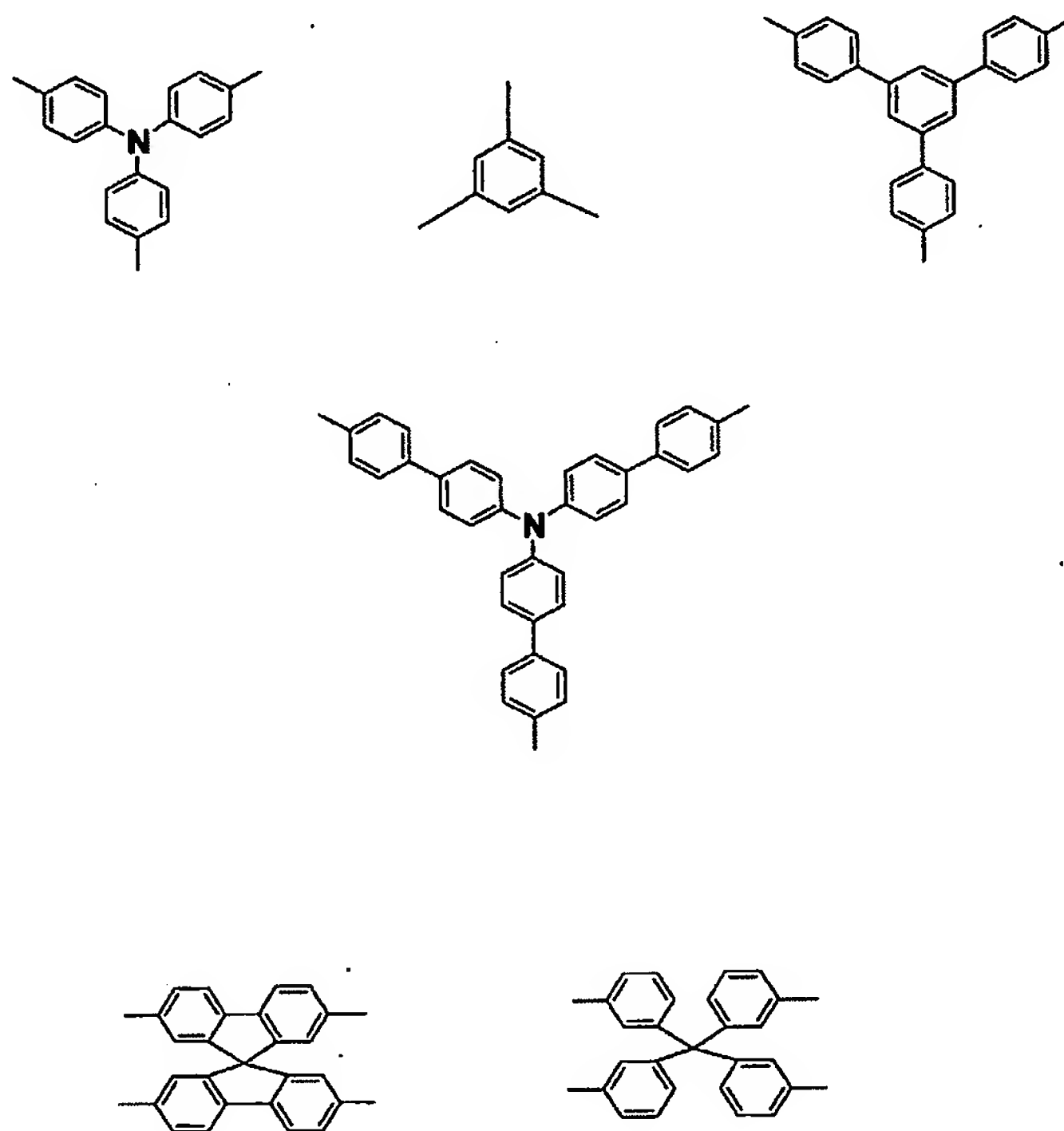


wherein

$R_{19}$ - $R_{22}$  are same or different and are selected from alkyl,  
heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and  $NR^5$ ,  
 $R^5$  is H or an alkyl; and

o and p are numbers of substituents on the benzene rings and are same or different and each of o and p is in a range of 0-3.

In one embodiment of the invention, the second monomeric unit is a branching monomeric unit having more than two linkage sites. Examples of suitable branching monomeric units include, but are not limited to:



In the copolymer of the invention, more than one of the second monomeric unit can be present with the first monomeric unit. For example, the copolymer can have the formula



wherein:

the first monomeric unit has Formula I as described above;

the ED, SE, HT, and branching units are as defined above;

q is an integer; and

r, s, t, and u are 0 or an integer, with the proviso that at least one of

r, s, t, and u is an integer.

The relative molar proportion of first monomeric unit to the at least one second monomeric unit(s) can be from 99.9:0.1 to 1:99 or 99.5:0.5 to 10:90; alternatively 99:1 to 20:80, and further alternatively 99:1 to 50:50.

The incorporation of the monomers in the formation of the polymer can be random or controlled, resulting in copolymers which include, but are not limited to, random copolymers, alternating copolymers and block copolymers.

5           The copolymers of the invention, generally comprise at least 3 first monomeric units. In one embodiment, the copolymer comprises at least 10 first monomeric units. In one embodiment, the copolymer comprises at least 50 first monomeric units.

10           In the copolymers of the invention, the degree of polymerization is generally at least 5. In one embodiment, the degree of polymerization is at least 10. In one embodiment, the degree of polymerization is at least 50.

#### Synthesis

15           The copolymers of the invention can generally be prepared by three known synthetic routes. In the first synthetic method, as described in Yamamoto, *Progress in Polymer Science*, Vol. 17, p 1153 (1992), the dihalo derivatives of the monomeric units are reacted with a stoichiometric amount of a zerovalent nickel compound, such as bis(1,5-cyclooctadiene)nickel(0). In the second method, as described in Colon et al., *Journal of Polymer Science, Part A, Polymer chemistry Edition*, Vol. 28, p. 367 (1990). The dihalo derivatives of the monomeric units are reacted with catalytic amounts of Ni(II) compounds in the presence of stoichiometric amounts of a material capable of reducing the divalent nickel ion to zerovalent nickel. Suitable materials include zinc, 25 magnesium, calcium and lithium. In the third synthetic method, as described in US Patent 5,962,631, and published PCT application WO 00/53565, a dihalo derivative of one monomeric unit is reacted with a derivative of another monomeric unit having two reactive groups selected from boronic acid, boronic acid esters, and boranes, in the presence of a 30 zerovalent palladium catalyst, such as tetrakis(triphenylphosphine)Pd. The di-tosylate derivatives of the monomeric units can also be used.

35           In some embodiments of the invention, the copolymer can be reacted with an end-capping compound to convert the reactive end group to a non-reactive end group. The end-capping compound is generally added to a preformed polymer and ends the polymerization reaction. The end-capping compound is generally an aromatic compound having a single reactive group, such as an aromatic ring having a single halide group or boronic acid or ester group. Examples of suitable end-capping

compounds include 9-bromoanthracene, 4-bromo-1,2-dimethoxybenzene, 1-bromopyrene, iodobenzene, bromobenzene, 2-bromo-9-fluorenone, and benzenboronic acid. The end-capping group may also be designed to add functionality, such as charge transport properties and color shifting. It may also affect interchain aggregation.

The copolymers of the invention can be used in electronic devices. FIG. 1 illustrates an exemplary electronic device 100 that includes an active layer positioned between two electrical contact layers. The electronic device 100 includes a hole transport layer 120 located between the active layer 130 and an anode layer 110. An optional electron transport layer 140 is located between the active layer 130 and a cathode layer 150. Depending on the application of the device 100, the active layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, phototubes, and photovoltaic cells, as described in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc., 1966). The device is not limited with respect to system, driving method, and utility mode. The polymers may be used as part of an organic active layer, hole-transport layer, or electron-transport layer in an organic light-emitting diode ("OLED") of a display. When used in OLEDs, some of the best device performances to date including high efficiency and blue color purity have been achieved.

The device may include a support or substrate (not shown) that can be adjacent to the anode layer 110 or the cathode layer 150. Most frequently, the support is adjacent the anode layer 110. The support can be flexible or rigid, organic or inorganic. Generally, glass or flexible organic films are used as a support. The anode layer 110 is an electrode that is more efficient for injecting holes compared to the cathode layer 150. The anode can include materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode layer 110 is to be light transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, may be used. Some non-limiting, specific examples of materials for anode layer 110 include indium-tin-oxide ("ITO"), aluminum-tin-oxide, gold, silver,

copper, nickel, and selenium. The anode may also comprise an organic material such as polyaniline.

The anode layer 110 may be formed by a chemical or physical vapor deposition process or spin-cast process. Chemical vapor deposition  
5 may be performed as a plasma-enhanced chemical vapor deposition ("PECVD") or metal organic chemical vapor deposition ("MOCVD"). Physical vapor deposition can include all forms of sputtering, including ion beam sputtering, as e-beam evaporation and resistance evaporation. Specific forms of physical vapor deposition include rf magnetron sputtering  
10 or inductively-coupled plasma physical vapor deposition ("IMP-PVD"). These deposition techniques are well known within the semiconductor fabrication arts.

Examples of materials which may facilitate hole-injection/transport comprise N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-  
15 diamine (TPD) and bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP); hole-transport polymers such as polyvinylcarbazole (PVK), (phenylmethyl)polysilane, poly(3,4-ethylenedioxythiophene) (PEDOT), and polyaniline (PANI), or the like; electron and hole-transporting materials such as 4,4'-N,N'-dicarbazole  
20 biphenyl (BCP); or light-emitting materials with good hole-transport properties such as chelated oxinoid compounds, including tris(8-hydroxyquinolato)aluminum (Alq<sub>3</sub>) or the like. In some embodiments, if the conductivity of the hole-injection/transport layer 120 can be made similar to anode layer 110, the anode layer 110 may not be  
25 required and the hole-injection/transport layer 120 can act as the anode for the electronic device.

The hole-injection/transport layer 120 can be formed using any conventional means, including spin-coating, casting, and printing, such as gravure printing. The layer can also be applied by ink jet printing, thermal  
30 patterning, or chemical or physical vapor deposition.

Usually, the anode layer 110 and the hole-injection/transport layer 120 are patterned during the same lithographic operation. The pattern may vary as desired. The layers can be formed in a pattern by, for example, positioning a patterned mask or resist on the first flexible  
35 composite barrier structure prior to applying the first electrical contact layer material. Alternatively, the layers can be applied as an overall layer (also called blanket deposit) and subsequently patterned using, for example, a patterned resist layer and wet chemical or dry etching techniques. Other



processes for patterning that are well known in the art can also be used. When the electronic devices are located within an array, the anode layer 110 and hole-injection/transport layer 120 typically are formed into substantially parallel strips having lengths that extend in substantially the same direction.

The polymers of the invention have particular utility in the active layer 130. This layer can be applied from solutions by any conventional technique, including spin-coating, casting, and printing.

Optional layer 140 can function both to facilitate electron-injection/transport, and also serve as a buffer layer or confinement layer to prevent quenching reactions at layer interfaces. More specifically, layer 140 may promote electron mobility and reduce the likelihood of a quenching reaction if layers 130 and 150 would otherwise be in direct contact.

Examples of materials which may facilitate hole-injection/transport comprise metal-chelated oxinoid compounds (e.g., Alq<sub>3</sub> or the like); phenanthroline-based compounds (e.g., 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ("DDPA"), 4,7-diphenyl-1,10-phenanthroline ("DPA"), or the like); azole compounds (e.g., 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole ("PBD" or the like), 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole ("TAZ" or the like); other similar compounds; or any one or more combinations thereof. Alternatively, optional layer 140 may be inorganic and comprise BaO, LiF, Li<sub>2</sub>O, or the like.

The electron-injection/transport layer 140 can be formed using any conventional means, including spin-coating, casting, and printing. The layer can also be applied by ink jet printing, thermal patterning, or chemical or physical vapor deposition.

The cathode layer 150 is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode layer 150 can be any metal or nonmetal having a lower work function than the first electrical contact layer (in this case, the anode layer 110). Materials for the second electrical contact layer can be selected from alkali metals of Group 1 (e.g., Li, Na, K, Rb, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, the rare earths, the lanthanides (e.g., Ce, Sm, Eu, or the like), and the actinides. Materials such as aluminum, indium, calcium, barium, yttrium, and magnesium, and combinations, may also be used. Specific non-limiting examples of materials for the cathode layer 150



include barium, lithium, cerium, cesium, europium, rubidium, yttrium, magnesium, and samarium.

The cathode layer 150 is usually formed by a chemical or physical vapor deposition process. In general, the cathode layer will be patterned, as discussed above in reference to the anode layer 110 and optional conductive polymer layer 120. If the device lies within an array, the cathode layer 150 may be patterned into substantially parallel strips, where the lengths of the cathode layer strips extend in substantially the same direction and substantially perpendicular to the lengths of the anode layer strips. Electronic elements called pixels are formed at the cross points (where an anode layer strip intersects a cathode layer strip when the array is seen from a plan or top view).

In other embodiments, additional layer(s) may be present within organic electronic devices. For example, a layer (not shown) between the conductive polymer layer 120 and the active layer 130 may facilitate positive charge transport, band-gap matching of the layers, function as a protective layer, or the like. Similarly, additional layers (not shown) between the active layer 130 and the cathode layer 150 may facilitate negative charge transport, band-gap matching between the layers, function as a protective layer, or the like. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 110, the conductive polymer layer 120, the active layer 130, and cathode layer 150, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers may be determined by balancing the goals of providing a device with high device efficiency with the cost of manufacturing, manufacturing complexities, or potentially other factors.

Although not meant to limit, the different layers may have the following range of thicknesses: inorganic anode layer 110, usually no greater than approximately 500 nm, for example, approximately 10-200 nm; conductive polymer layer 120, usually no greater than approximately 250 nm, for example, approximately 20-200 nm; active layer 130, usually no greater than approximately 1000 nm, for example, approximately 10-80 nm; optional layer 140, usually no greater than approximately 100 nm, for example, approximately 20-80 nm; and cathode layer 150, usually no greater than approximately 100 nm, for example, approximately 30-500 nm. If the anode layer 110 or the cathode layer 150

needs to transmit at least some light, the thickness of such layer may not exceed approximately 100 nm.

In polymer light emitting diodes, electrons and holes, injected from the cathode 150 and anode 110 layers, respectively into the active polymer layer 130, form negative and positively charged polarons in the polymer. These polarons migrate under the influence of the applied electric field, forming a polaron exciton with an oppositely charged species and subsequently undergoing radiative recombination. A sufficient potential difference between the anode and cathode, usually less than approximately 12 volts, and in many instances no greater than approximately 5 volts, may be applied to the device. The actual potential difference may depend on the use of the device in a larger electronic component. In many embodiments, the anode layer 110 is biased to a positive voltage and the cathode layer 150 is at substantially ground potential or zero volts during the operation of the electronic device. A battery or other power source(s) may be electrically connected to the electronic device as part of a circuit but is not illustrated in FIG. 1.

The invention will now be described in greater detail by reference to the following non-limiting examples.

20

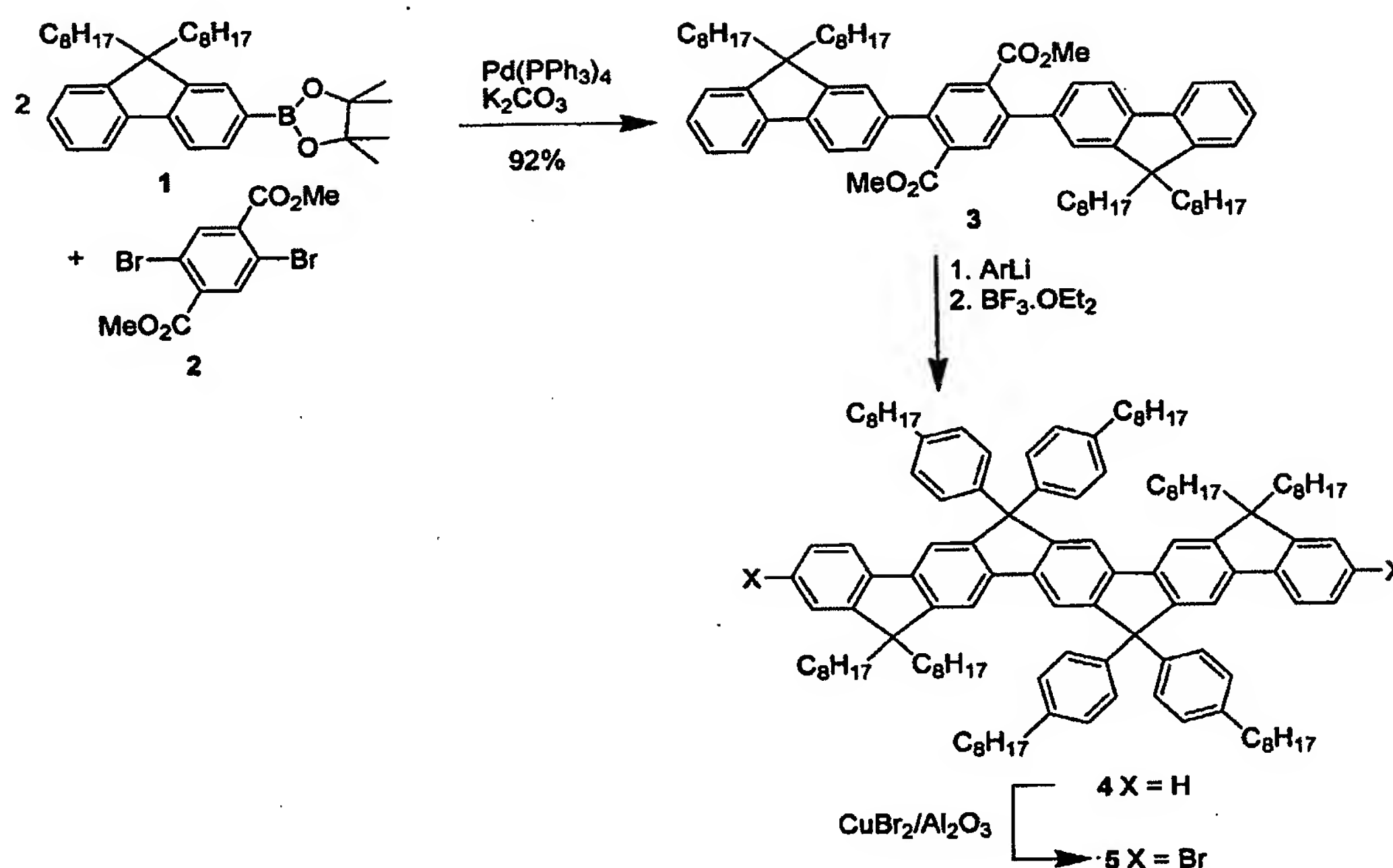
### EXAMPLES

#### Example 1

This example illustrates the preparation of a first monomer which can be used to prepare a copolymer of the invention..

As shown in the scheme below, Suzuki coupling of the fluorene-2-boronate ester 1, with the dibromoterephthalate 2 generated an intermediate, the pentaphenylenediester 3 in 92 % yield. Addition of an excess of 4-alkylphenyl lithium produced a diol which was facilely ring-closed using  $\text{BF}_3$  etherate to generate the ladder-type pentaphenylene 4 (95 %). Bromination of 4 using  $\text{CuBr}_2$  on alumina<sup>23</sup> gave the monomer 5 (91 %).

30



### Synthesis of the pentaphenylene diester 3.

The boronate ester 1 (4.65 g, 9.0 mmol), diester 2 (1.52 g, 4.39 mmol),  $\text{K}_2\text{CO}_3$  (1.21 g, 8.8 mmol) were dissolved in THF (40 mL) and water (20 mL) in a 100 mL schlenk flask. The solution was purged with argon for twenty minutes and then tetrakis(triphenylphosphine)palladium (152 mg, 0.03 equiv) was added and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and after 16 h was worked up. The cooled mixture was extracted with diethyl ether, and the extract was washed with saturated salt and then dried over  $\text{MgSO}_4$ . The crude product so obtained was purified by chromatography on silica using 0-5 % ethylacetate in hexane as eluent. The product 3 was isolated as a thick viscous oil (3.94 g, 92 %).  $^1\text{H}$  NMR: ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.88 (s, 2H) 7.78 (m, 4H) 7.40-7.33 (m, 10H) 3.65 (s, 6H) 2.00 (t, 8H,  $J = 8.5\text{ Hz}$ ) 1.21-1.07 (m, 40H) 0.62-0.83 (m, 20H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  169.26, 151.74, 151.62, 141.89, 141.56, 141.43, 139.54, 134.37, 132.44, 128.02, 127.82, 127.59, 123.84, 123.73, 120.55, 120.29, 55.96, 52.78, 41.16, 32.54, 30.81, 30.05, 29.99, 24.56, 23.35, 14.58 ppm. FDMS:  $m/z$  971.3 Elemental Analysis: Calculated C 84.07 H 9.34 Found C 84.12 H 9.32.

Synthesis of the ladder-type pentaphenylene 4.

- a) A solution of 4-octylbromobenzene (3.05 mL, 3.4 g, 12.6 mmol) in dry THF (40 mL) in a 250 mL schlenk flask, was cooled to -78 °C in an acetone/dry ice bath. n-Butyllithium in hexane (8.0 mL, 1.6 M, 12.8 mmol) was then added and stirred for 20 minutes. Then a solution of the diester 5 (2.05 g, 2.1 mmol) in dry THF (40 mL) was added dropwise with stirring and the solution was slowly allowed to warm to room temperature. The mixture was stirred overnight and then the quenched with brine. The mixture was extracted with diethyl ether, and the extract was washed with salt and dried over MgSO<sub>4</sub>. The crude product was chromatographed on silica using 0-5 % ethylacetate in hexane as eluent to give the diol as a thick viscous oil. (3.39 g, 96 %). <sup>1</sup>H NMR: δ 7.61 (m, 2H) 7.45 (d, 2H, J = 7.6Hz) 7.29 (m, 6H) 7.12 (m, 16H) 6.76 (m, 4H) 6.69 (s, 2H) 3.11 (s, 2H) 2.61 (t, 8H, J = 7.6Hz) 1.77-0.45 (m, 128H) ppm. <sup>13</sup>C NMR: δ 151.63, 151.23, 146.41, 144.19, 142.74, 141.71, 141.21, 141.05, 139.29, 136.29, 129.29, 128.76, 128.58, 127.93, 127.48, 124.32, 123.63, 120.35, 120.22, 83.91, 55.75, 40.55, 36.30, 32.72, 32.60, 32.45, 30.73, 30.30, 30.12, 30.09, 30.07, 30.04, 24.56, 23.46, 23.39, 14.65, 14.61 ppm. FDMS: m/z 1668.3.
- b) ring-closure: The diol (3.30 g, 1.98 mmol) was dissolved in dichloromethane (30 mL, used as purchased) and BF<sub>3</sub> etherate (0.20 mL) was added with stirring at room temperature. The colorless solution turned deep brown immediately upon addition and became light yellow within minutes. After 10 minutes, methanol (50 mL) was added to the solution whereupon the pentamer 4 started to precipitate as a colourless solid. The mixture was stirred for 12 h and then the solid was collected by filtration, washed with methanol and dried. The product was redissolved in dichloromethane and precipitated again by addition of methanol. Isolated yield of 4 = 3.06 g (95 %). <sup>1</sup>H NMR: δ 7.83 (s, 2H) 7.63 (m, 6H) 7.33-7.11 (m, 22H) 2.58 (t, 8H, J = 7.6Hz) 2.02 /t, 3H, J = 7.9Hz) 1.63-0.62 (m, 120H) ppm. <sup>13</sup>C NMR: δ 152.80, 152.05, 151.88, 151.55, 144.35, 142.29, 141.83, 140.91, 140.87, 140.25, 129.11, 128.97, 127.63, 127.37, 123.65, 120.34, 118.16, 117.82, 115.35, 65.15, 55.61, 41.39, 36.28, 32.65, 32.55, 32.30, 30.82, 30.30, 30.22, 30.03, 30.01, 29.98, 24.67, 23.43, 23.34, 14.64, 14.60 ppm. FDMS: m/z 1633.2 . Elemental Analysis: Calculated C 89.75 H 10.25 %; Found: C 89.77 H 10.19 %.

### Synthesis of monomer 5.

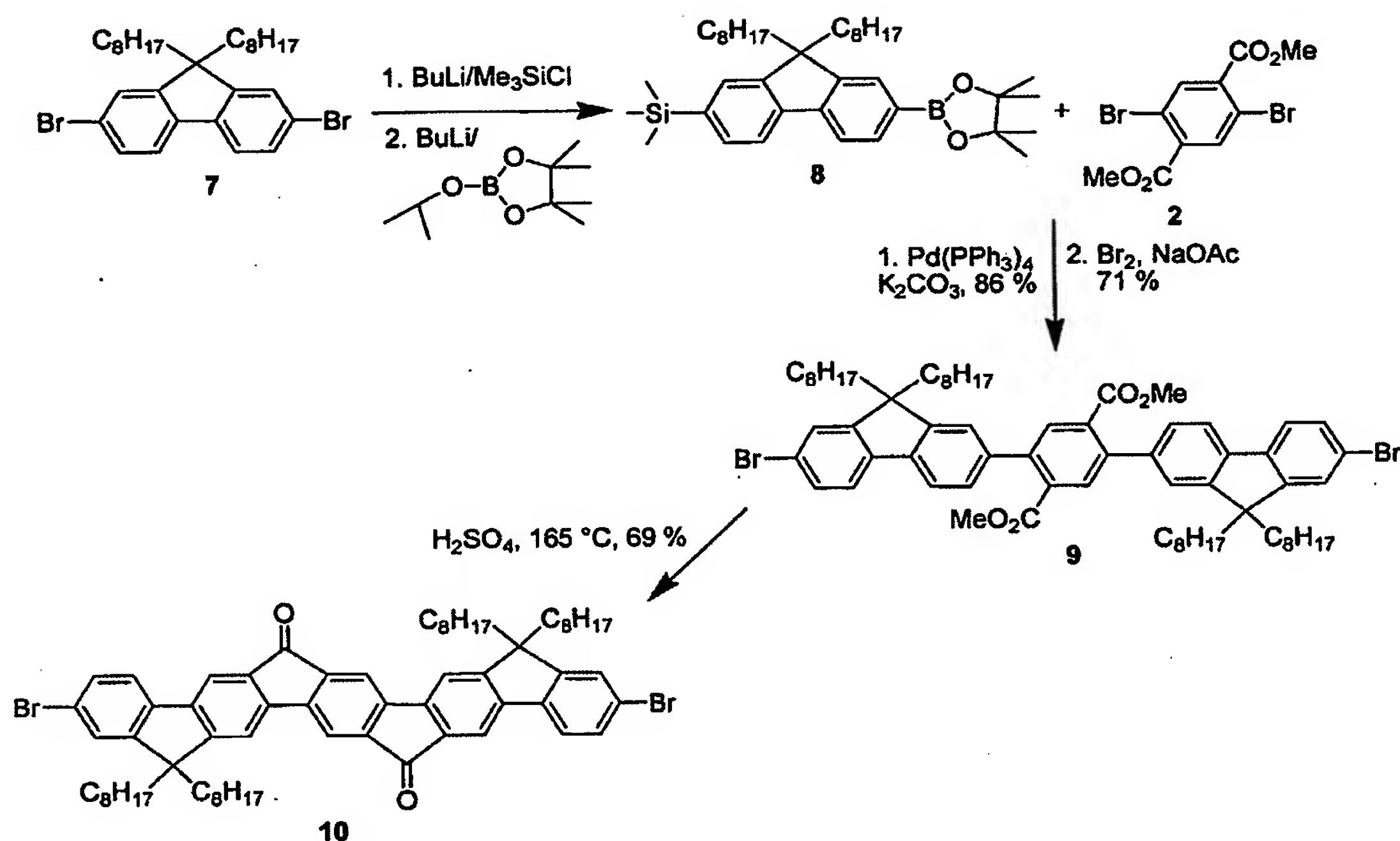
The pentaphenylene 4 (0.80 g, 0.49 mmol) was added to carbon tetrachloride (30 mL) in a 100 mL round-bottomed flask, followed by CuBr<sub>2</sub> on alumina (2.0 g).<sup>23</sup> The reaction was heated under reflux with stirring and monitored by FDMS, which showed nearly quantitative formation of the dibromide after 14 h. The reaction mixture was concentrated, and the residue was loaded on silica and chromatographed on silica using hexane as eluent. The product 5 was isolated as a light yellow solid, (0.80 g, 91 %). <sup>1</sup>H NMR: δ 7.82 (s, 2H) 7.66 (d, 4H, J = 9.1Hz) 7.42 (m, 6H) 7.24 (d, 8H, J = 8.2Hz) 7.12 (d, 8H, J = 8.2Hz) 2.58 (t, 8H, J = 7.3Hz) 2.00 (t, 8H, J = 7.6Hz) 1.59 (m, 8H) 1.31-0.78 (m, 112H) ppm. <sup>13</sup>C NMR: δ 154.19, 152.90, 152.30, 151.23, 144.17, 142.38, 140.97, 140.85, 140.76, 140.69, 130.52, 129.14, 128.95, 126.92, 121.79, 121.51, 118.29, 117.97, 115.44, 65.17, 55.99, 41.28, 36.26, 32.65, 32.53, 32.29, 30.73, 30.69, 30.29, 30.22, 30.00, 29.97, 24.62, 23.43, 23.35, 14.64, 14.60 ppm. FDMS: m/z 1780.50. Elemental Analysis: Calculated C 81.84 H 9.23 %; Found: 81.99 H 9.24 %.

### Example 3

This example illustrates the preparation of a second monomer which can be used to form the copolymer of the invention.

As shown in the scheme below, 2,7-Dibromo-9,9-dioctylfluorene 7 was converted via the monosilyl compound to the boronate 8. Suzuki coupling of this with the terephthalate 2 gave a crude disilylpentaphenylene in 86 % yield, which was converted to the dibromide 9 with sodium acetate and bromine (72 %). The monomers 5 could then be obtained by addition of aryllithium and ring closure, but in view of the longer synthesis and lower overall yield, this route is inferior to the previously described route. Treatment of 9 with concentrated sulphuric acid at 165 °C induced a double intramolecular Friedel-Crafts acylation to produce the desired diketone 10 in 65 % yield. By contrast treatment of the unbrominated diester 3 under the same condition gave incomplete ring closure.





#### Synthesis of 7-trimethylsilyl-9,9-di-n-octylfluorene-2-boronate 8.

- 5 n-Butyllithium in hexane (6.0 mL, 1.6 M, 9.6 mmol) was added to a solution of 2,7-dibromo-9,9-di-n-octylfluorene (7) (5.00 g, 9.13 mmol) in dry THF (50 mL) in a schlenk flask at -78 °C and the mixture was stirred for 20 minutes. Then chlorotrimethylsilane (1.5 mL, 1.29 g, 1.3 equiv) was added and the reaction was allowed to slowly warm to room temperature.
- 10 The mixture was stirred overnight and the reaction was quenched with saturated brine. The product was extracted into diethyl ether, and the extract was washed with brine and dried over MgSO<sub>4</sub>. The crude product was chromatographed on silica using hexane as eluent to give 2-bromo-7-trimethylsilyl-9,9-di-n-octylfluorene as a colourless oil, (3.50 g, 71 %).
- 15 n-Butyllithium in hexane (4.4 mL, 1.6 M, mmol) was added to a solution of 2-bromo-7-trimethylsilyl-9,9-di-n-octylfluorene (3.47 g, 6.41 mmol) in dry THF (75 mL) in a schlenk flask at -78 °C, and the mixture was stirred for 20 minutes. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.44 mL, 1.31 g, 7.04 mmol) was added and the reaction was stirred for
- 20 24 h after warming to room temperature. The reaction was then quenched with brine, and the product was extracted into diethyl ether. The extract was washed with brine and dried over MgSO<sub>4</sub>. The crude product was



chromatographed on silica using 0-3 % ethylacetate in hexane as eluent, to give **8** as a colourless solid (2.67 g, 71 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.73 (m, 4H) 7.51 (m, 2H) 1.99 (t, 4H,  $J = 8.2\text{Hz}$ ) 1.36-0.54 (m, 42H) 0.31 (s, 9H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  151.60, 151.34, 149.76, 145.29, 142.69, 141.07, 134.71, 133.01, 130.08, 129.03, 120.50, 120.25, 84.93, 56.22, 41.26, 33.01, 32.84, 31.11, 30.37, 25.98, 24.95, 23.85, 15.08, 0.01. FDMS  $m/z$  588.90.

#### Synthesis of dibromopentaphenylene **9**.

The boronate ester **8** (2.45 g, 4.16 mmol), the diester **9** (697 mg, 1.98 mmol), and  $\text{K}_2\text{CO}_3$  (821 mg) were dissolved in a mixture of THF (20 mL) and  $\text{H}_2\text{O}$  (10 mL) in a schlenk flask and the mixture was purged with argon for 20 minutes. To this tetrakis(triphenylphosphine)palladium (114 mg, 0.05 equiv) was added and the mixture was heated at  $85^\circ\text{C}$  for 20 h. The cooled mixture was extracted with diethyl ether, and the extract was washed with brine and dried over  $\text{MgSO}_4$ . The residue was chromatographed on silica using 0-3 % ethylacetate in hexane to give the crude disilylpentaphenylene (1.89 g, 86 %).

In a schlenk flask, the diester **2** (1.89 g, 1.69 mmol) was added to dry THF (34 mL) along with anhydrous sodium acetate (278 mg, 2 equiv) and cooled to  $0^\circ\text{C}$ . Bromine (0.37 mL, 1.15 g, 4.2 equiv) was added and the mixture was stirred for 20 minutes. The reaction was quenched by addition of triethylamine (1.89 mL, 8 equiv) followed by an excess of aqueous  $\text{Na}_2\text{SO}_3$ . The product was extracted into diethyl ether, and the extract was washed with sodium sulfite solution and dried over  $\text{MgSO}_4$ . The residue was recrystallized from hot hexane to give the dibromide **9** as shiny colourless crystals (1.37 g, 72 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.87 (s, 2H) 7.77 (d, 2H,  $J = 7.9\text{Hz}$ ) 7.64 (d, 2H,  $J = 7.9\text{Hz}$ ) 7.53-7.31 (m, 8H) 3.64 (s, 6H) 1.99 (t, 8H,  $J = 8.8\text{Hz}$ ) 1.27-0.62 (m, 60H) ppm.  $^{13}\text{C}$  NMR:  $\delta$  169.06, 154.06, 151.27, 141.89, 140.58, 140.49, 140.05, 134.32, 132.51, 130.76, 128.06, 127.04, 123.87, 122.01, 121.96, 120.46, 56.36, 52.82, 41.08, 32.54, 30.74, 30.03, 29.99, 24.52, 23.36, 14.59 ppm. FDMS  $m/z$  1129.30  
Elemental Analysis: Calculated C 72.33 H 7.85 %; Found C 72.75 H 7.91 %.

#### Synthesis of dibromopentaphenylenedione **10**.

The dibromide **9** (1.37 g) was added to 40 mL of 80 %  $\text{H}_2\text{SO}_4$  (made from 4 mL  $\text{H}_2\text{O}$  and 36 mL conc.  $\text{H}_2\text{SO}_4$ ) and heated with stirring at  $165^\circ\text{C}$  for 3h during which time the white solid turned brown. The acid was decanted off and the product was extracted into dichloromethane, and

the extract was washed with sodium hydrogencarbonate solution and dried over  $\text{MgSO}_4$ . The crude product was purified by chromatography on silica using 0-3 % ethylacetate in hexane as eluent to give the diketone 10 as a grey solid (0.88 g, 69 %).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.97 (s, 2H) 7.86 (s, 2H) 7.65-7.49 (m, 8H) 2.03 (t, 8H,  $J = 8.5\text{Hz}$ ) 1.25-0.62 (m, 60H) ppm.

$^{13}\text{C}$  NMR:  $\delta$  192.91, 159.79, 153.77, 146.79, 144.19, 142.53, 140.81, 139.69, 134.70, 131.11, 127.10, 122.66, 122.21, 116.50, 116.38, 116.27, 56.96, 40.88, 32.53, 30.66, 29.97, 29.95, 24.60, 23.37, 14.60 ppm.

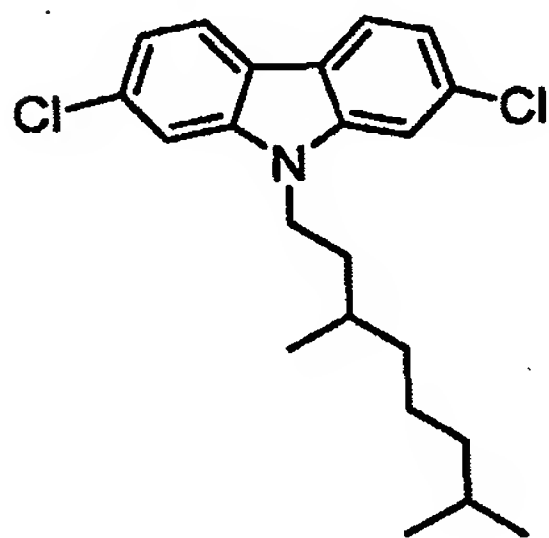
Elemental Analysis: Calculated C 74.42 H 7.57 %; Found C 74.63 H 7.60 %.

#### Example 4

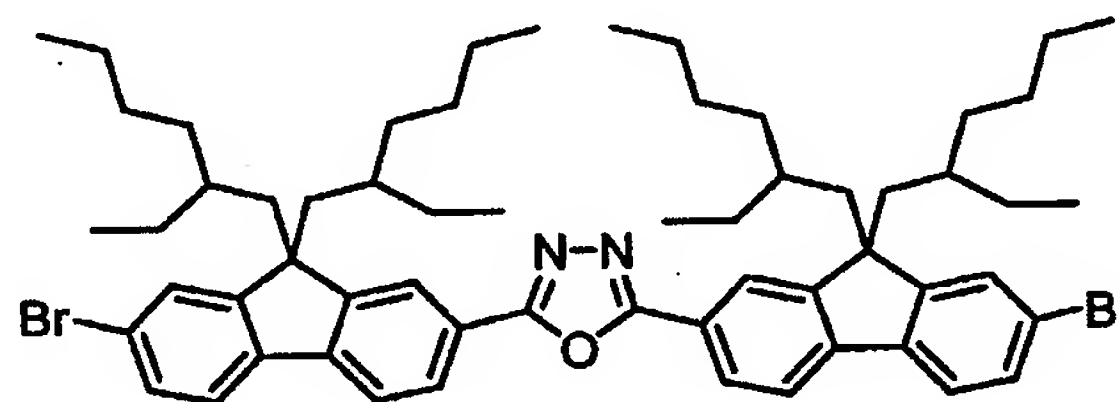
This example illustrates the preparation of a copolymer of the invention.

Comonomers:

Monomer 5 40 mol%



20 mol%



40 mol%

Under inert conditions, DMF (7 mL) will be added to a Schlenck tube equipped with a stirring bar and containing *bis*(1,5-cyclooctadiene)nickel (0) (1.612 g, 5.86 mmol), 2,2'-bipyridyl (0.915 g, 5.86 mmol), and 1,5-cyclooctadiene (0.634 g, 5.86 mmol). The ensuing deep blue/purple solution will be stirred at 60 °C for 30 minutes, and then a solution of monomer 5 from Example 2 (2.065 g, 1.16 mmol), a second monomer, 2,5-bis-[7-bromo-9,9-bis-(2-ethylhexyl)-9H-fluoren-2-yl]-[1,3,4]oxadiazole (1.166 g, 1.16 mmol) a third monomer and 2,7-dichloro-9-(3,7-dimethyl-octyl)-9H-carbazole (0.218 g, 0.58 mmol) in toluene (28 mL) will be added via syringe. The reaction mixture will then be stirred at 75 °C for 24 h. The mixture will be cooled to room temperature and

precipitated into a solution of methanol (100 mL), acetone (100 mL) and concentrated hydrochloric acid (5 mL). After stirring for 2 hours, the mixture will be filtered. The solid residue will then be dissolved in chloroform, and again precipitated into a solution of methanol (100 mL),  
5 acetone (100 mL) and concentrated hydrochloric acid (5 mL). After stirring for 1 hour, the mixture will be filtered. The solid will again be dissolved in chloroform and precipitated in pure methanol. Finally the residue will be successively washed with methanol, water and methanol and dried in vacuo.

10

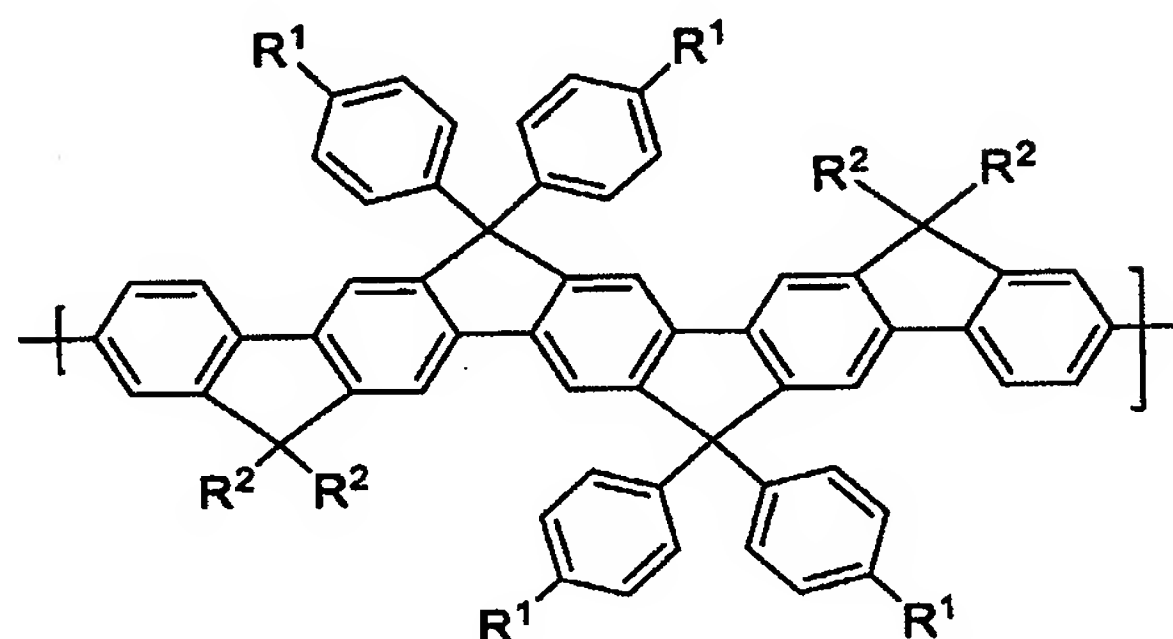
CLAIMS

What is claimed is:

1. A copolymer comprising at least one monomeric unit having

Formula I:

5



(I)

wherein:

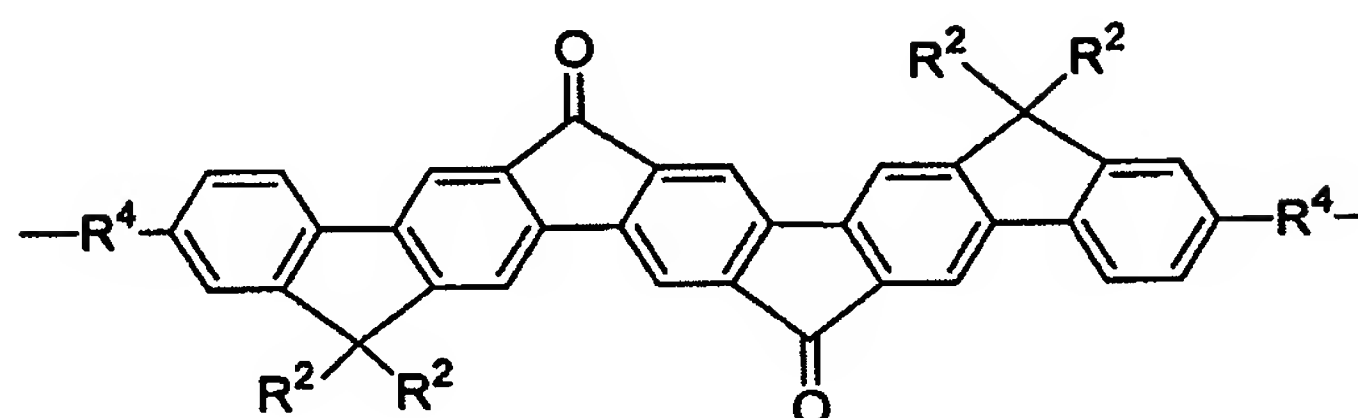
$R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

$R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

$R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

and at least one second monomeric unit comprising an aromatic group.

2. A copolymer according to Claim 1, wherein the second monomeric unit has Formula II:



5

(II)

wherein:

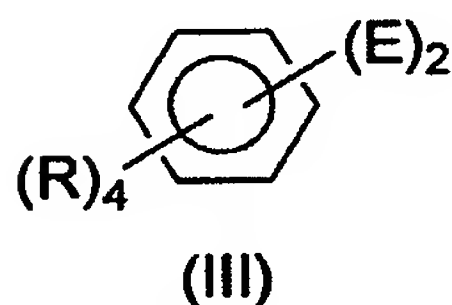
$R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

15

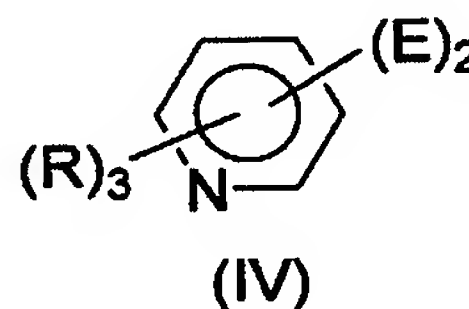
$R^4$  is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

3. A copolymer according to Claim 1, wherein the second monomeric unit has a formula selected from Formula III through Formula XII and combinations thereof,

20

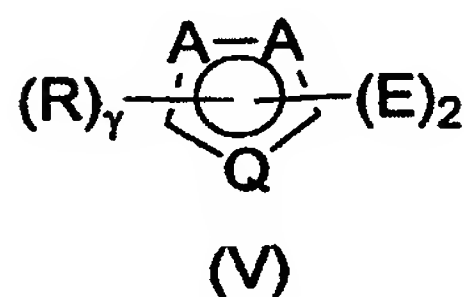


(III)

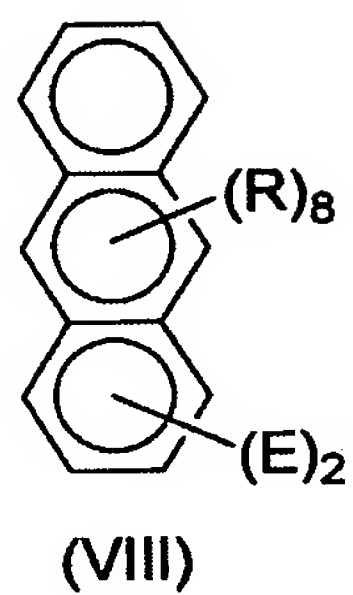
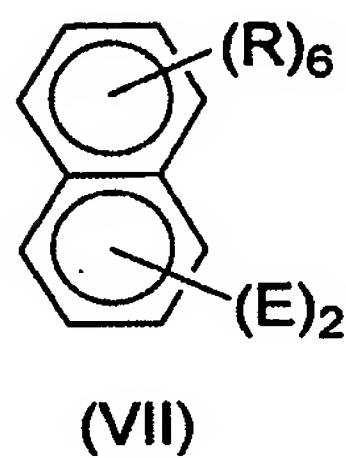
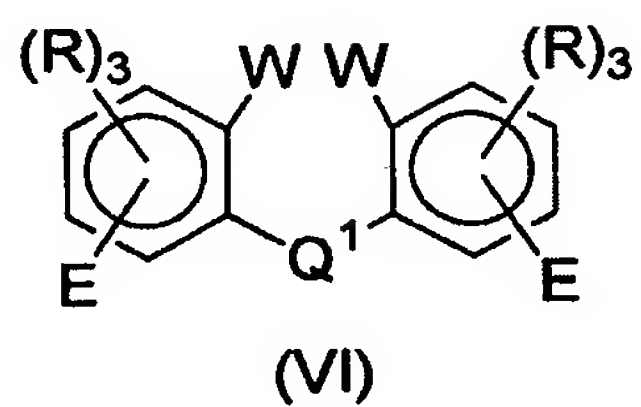


(IV)

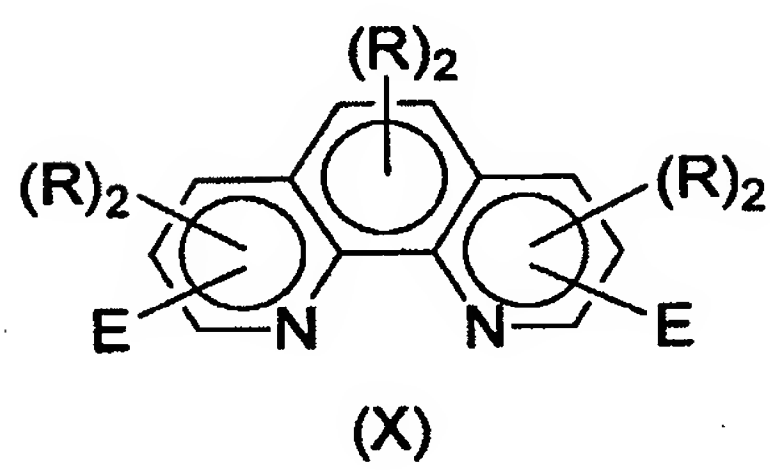
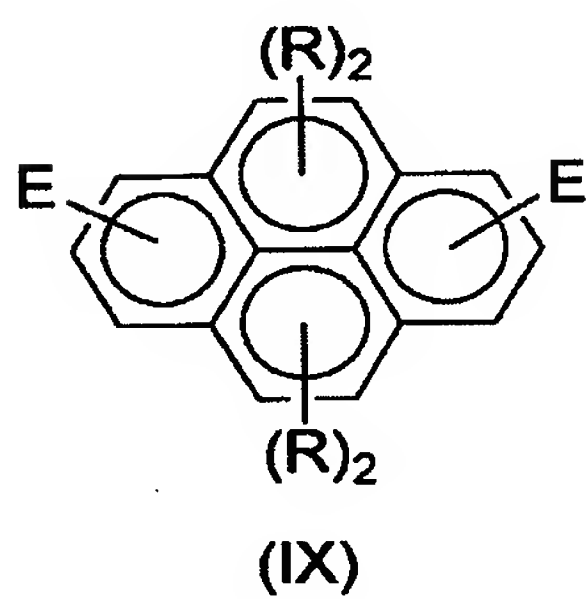
25



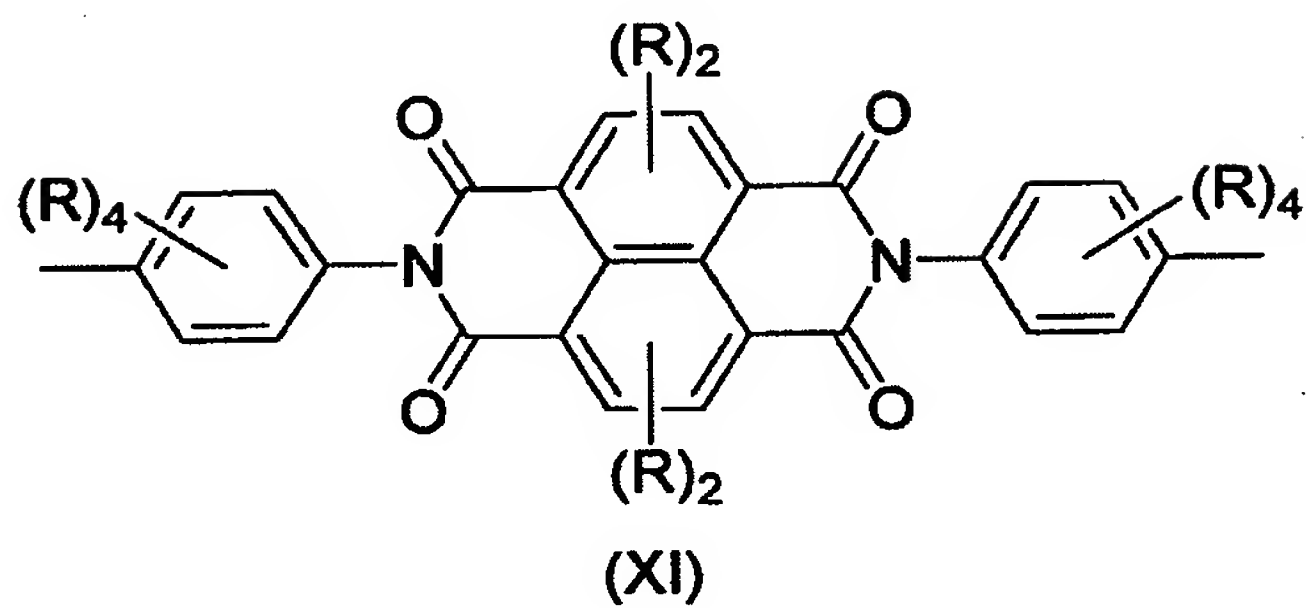
(V)



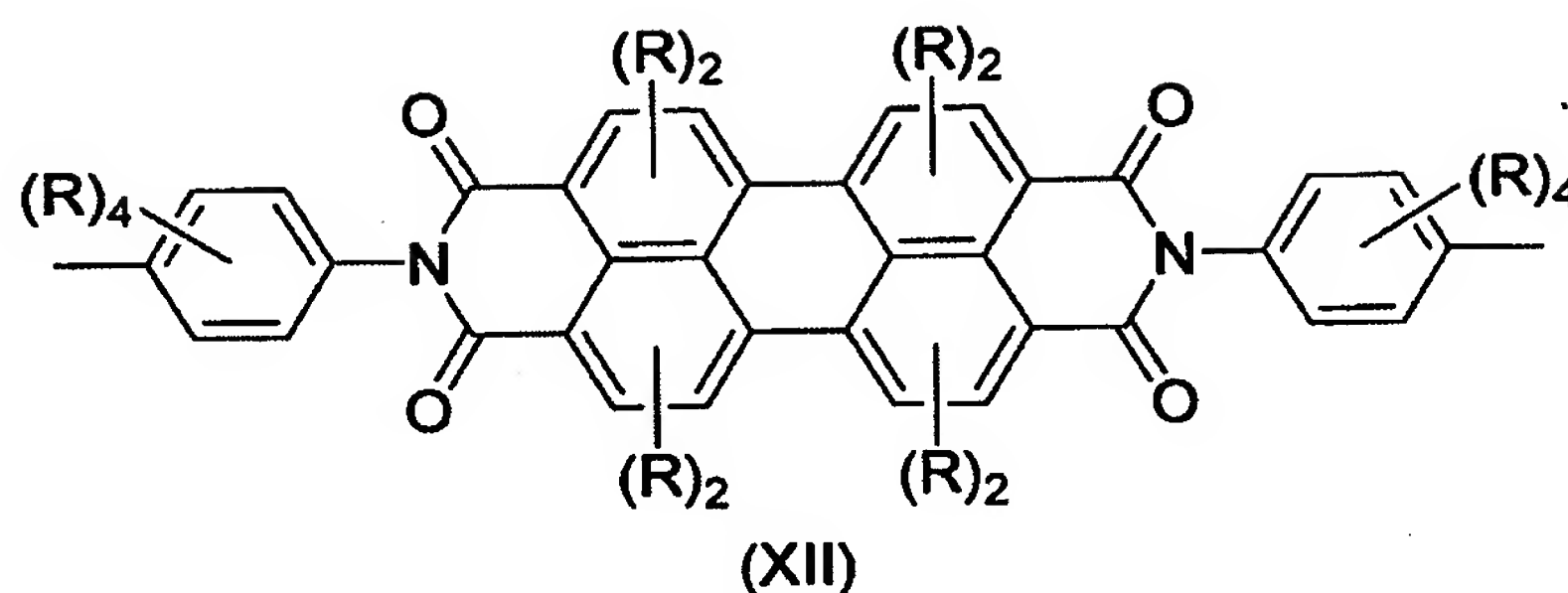
5



10







5 where:

in each of Formulae III through XII:

R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring;

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl

in each of Formulae III, IV, V, VI, VII, VIII, IX and X:

E can be the same or different at each occurrence and is a single bond or a linking group selected from arylene and heteroarylene; in Formula V:

A is independently at each occurrence C or N and γ is 0 or an integer selected from 1 or 2, such that when both A are N, then γ is 0; or when one of A is N and one of A is C, then γ is 1; or when both A are C, then γ is 2;

Q is O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

in Formula VI:

Q<sup>1</sup> is a carbonyl group, O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

$R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

W is H, alkyl or heteroalkyl; or both of W together can represent one single bond;  
in Formula VII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;

in Formula VIII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10-

positions;

in Formula IX:

a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8 position; and

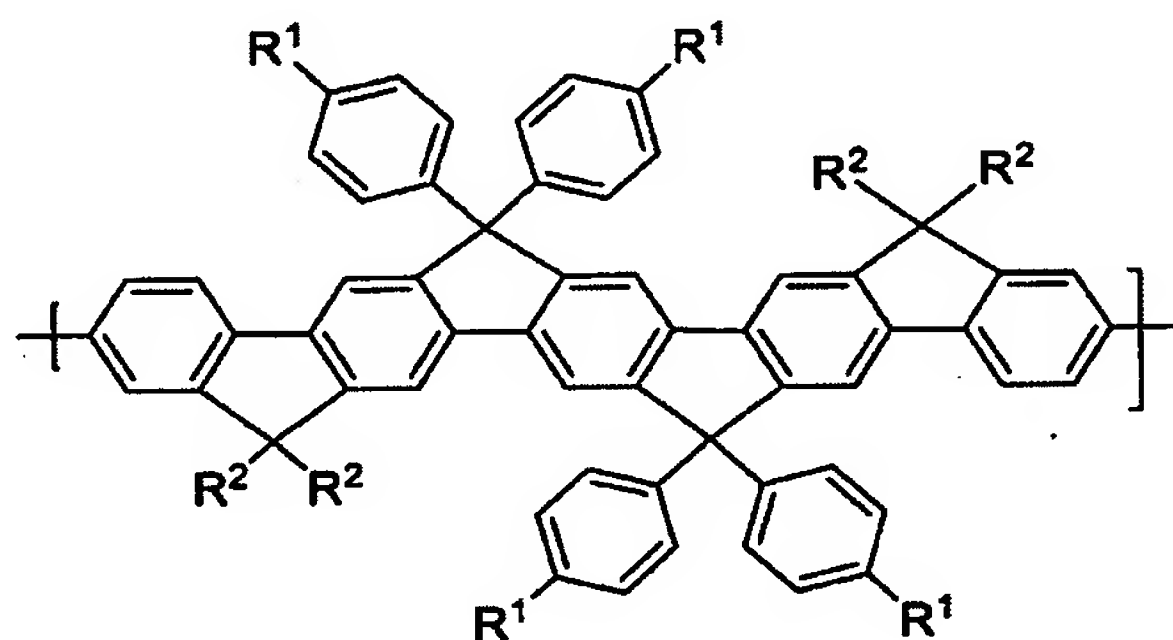
in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

4. A copolymer according to Claim 1, wherein  $R^1$  is a  $C_1$ - $C_{20}$  alkyl.

5. A copolymer according to Claim 1, wherein  $R^2$  is a  $C_1$ - $C_{20}$  alkyl.

6. An electronic device comprising an active layer positioned between two electrical contact layers, wherein the active layer comprises a copolymer comprising at least one monomeric unit having Formula I:



(I)

wherein:

$R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl,

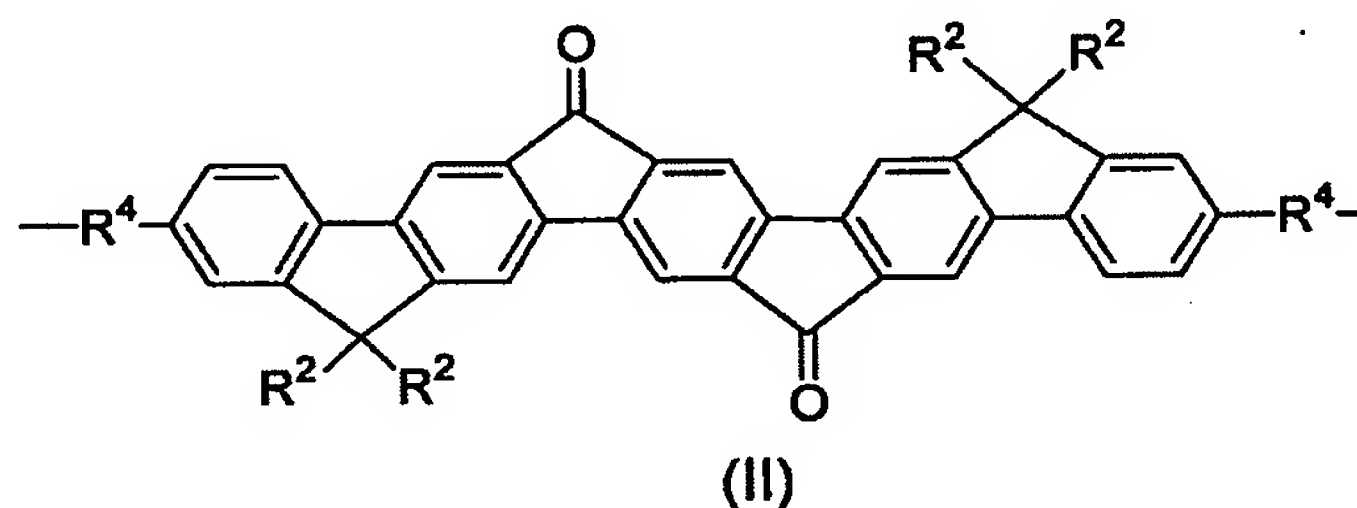
heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

$R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl,  $-CN$ ,  $-OR^3$ ,  $-CO_2R^3$ ,  $-SR^3$ ,  $-N(R^3)_2$ ,  $-P(R^3)_2$ ,  $-SOR^3$ ,  $-SO_2R^3$ , and  $-NO_2$ ; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

**R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl.**

15            7. An electronic device according to Claim 6, wherein the copolymer further comprises at least one second monomeric unit comprising an aromatic group.

8. An electronic device according to Claim 7, wherein the second monomeric unit has Formula II:

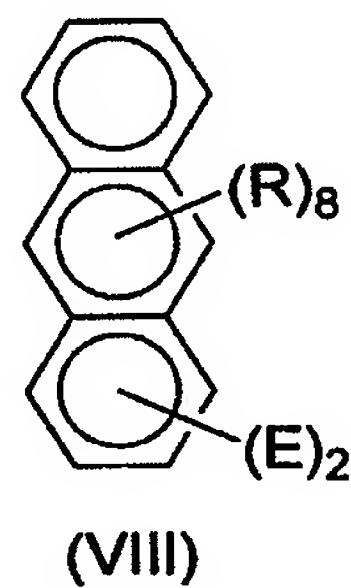
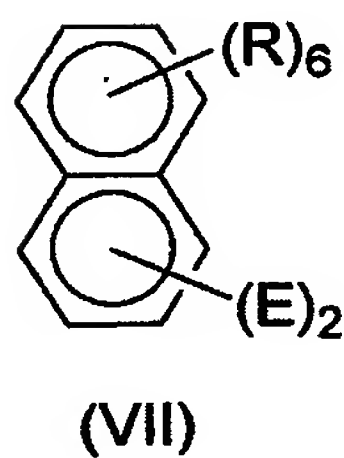
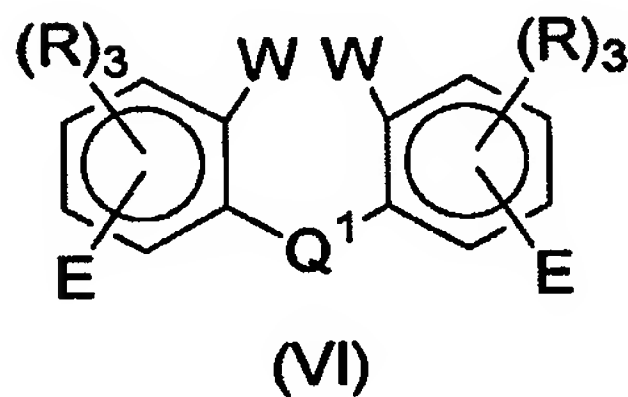
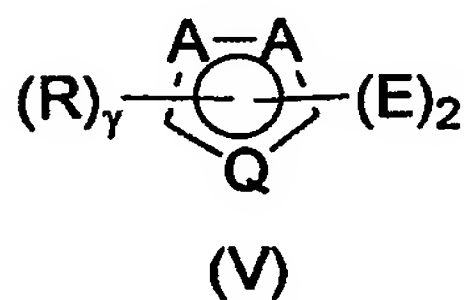
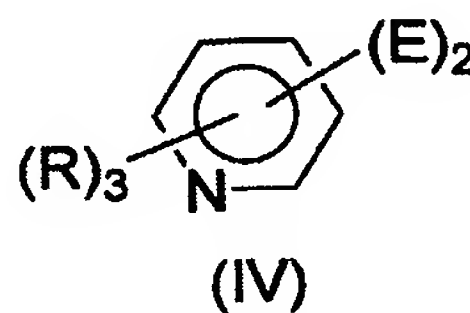
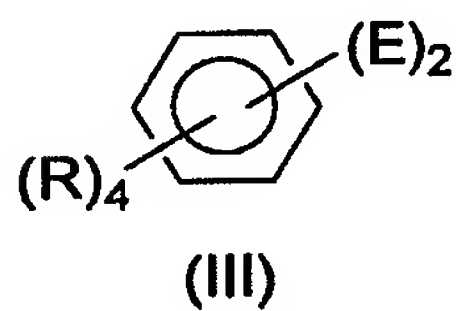


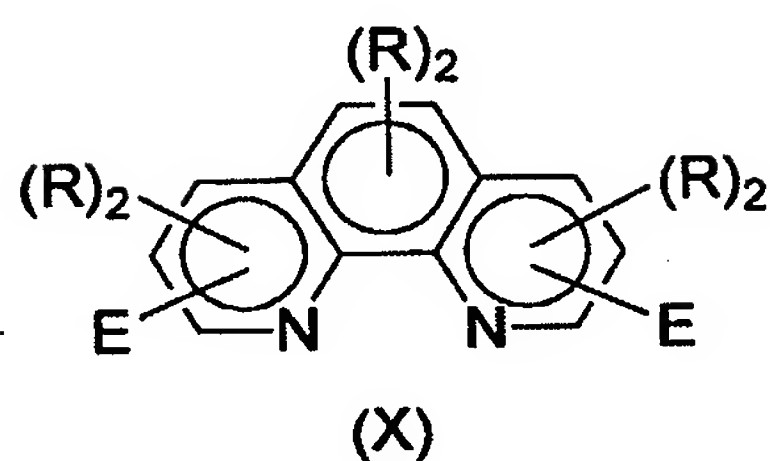
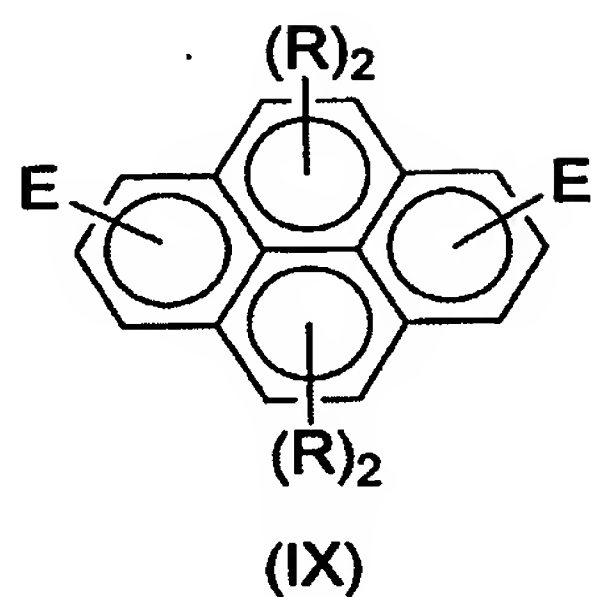
**wherein:**

25 R<sup>2</sup> is the same or different at each occurrence and is selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub> oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, 30 heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

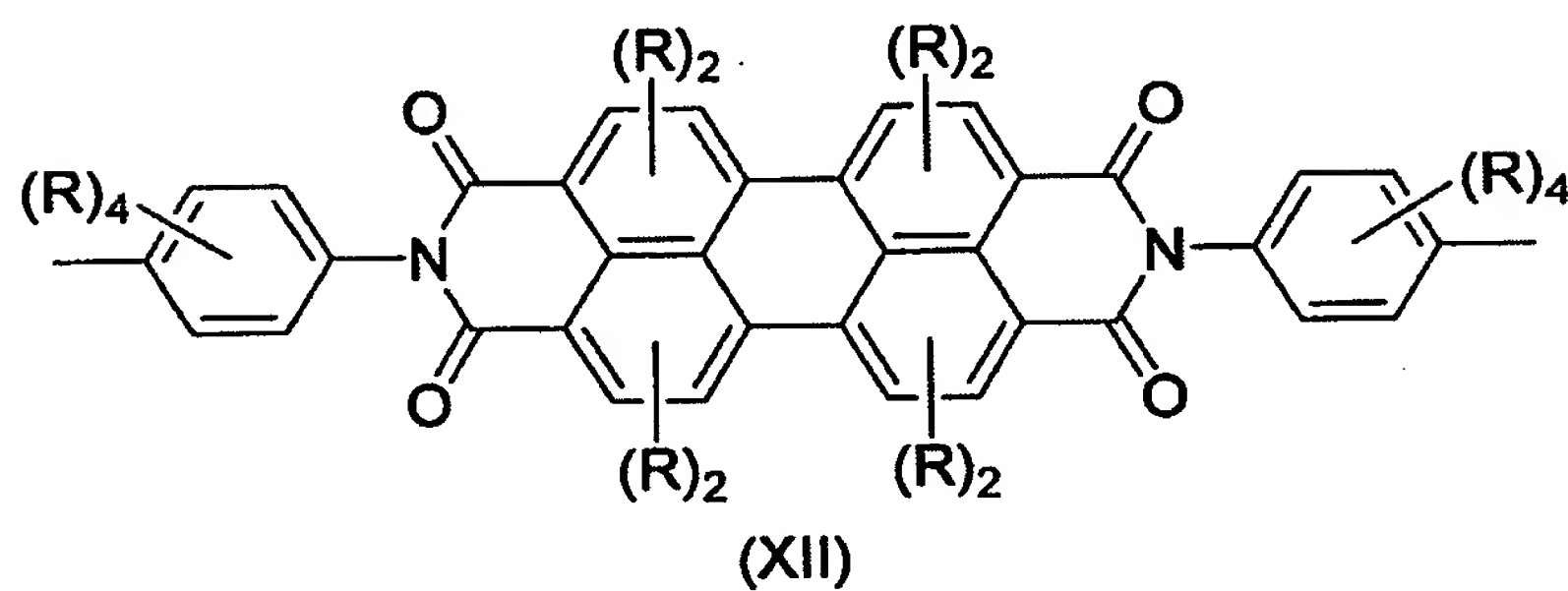
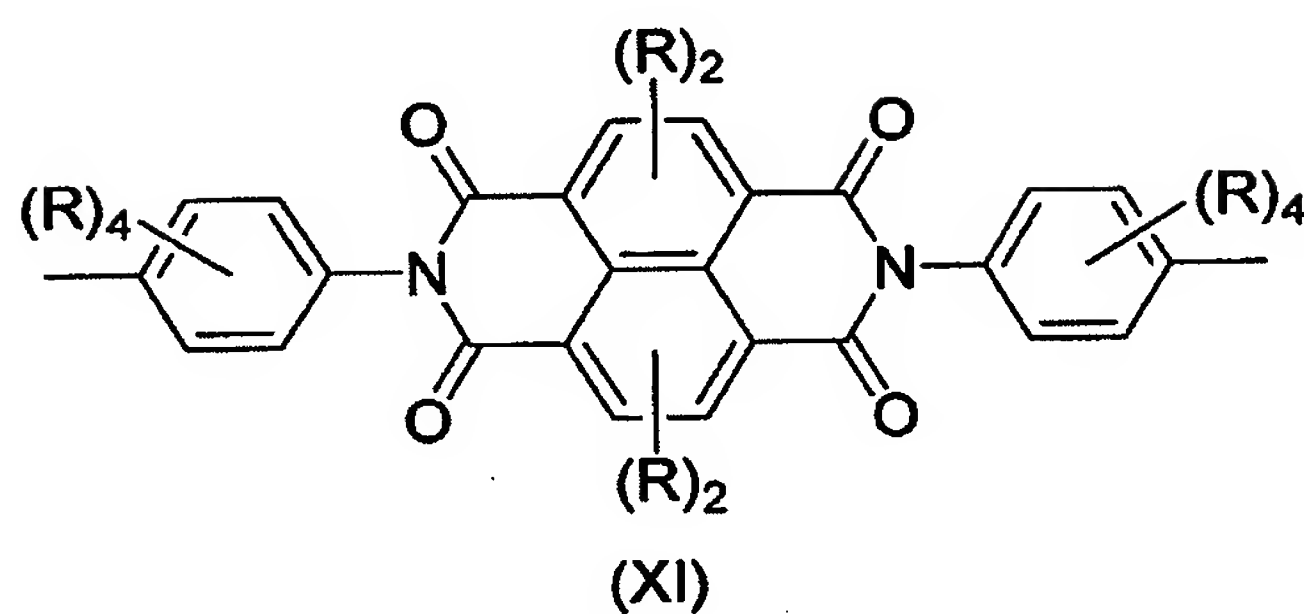
R<sup>4</sup> is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

9. An electronic device according to Claim 7, wherein the second monomeric unit has a formula selected from Formula III through Formula XII and combinations thereof,





5



10

where:

in each of Formulae III through XII:

15

R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>1</sub>-C<sub>20</sub> oxyalkyl, C<sub>2</sub>-C<sub>20</sub>

oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> oxyalkynyl, C<sub>1</sub>-C<sub>20</sub> fluorinated alkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated alkenyl, C<sub>1</sub>-C<sub>20</sub> fluorinated oxyalkyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkenyl, C<sub>2</sub>-C<sub>20</sub> fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring;

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl

10 in each of Formulae III, IV, V, VI, VII, VIII, IX and X:

E can be the same or different at each occurrence and is a single bond or a linking group selected from arylene and heteroarylene; in Formula V:

A is independently at each occurrence C or N and  $\gamma$  is 0 or an integer selected from 1 or 2, such that when both A are N, then  $\gamma$  is 0; or when one of A is N and one of A is C, then  $\gamma$  is 1; or when both A are C, then  $\gamma$  is 2;

Q is O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

20 in Formula VI:

Q<sup>1</sup> is a carbonyl group, O, S, SO<sub>2</sub>, or NR<sup>3</sup> where:

R<sup>3</sup> is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

W is H, alkyl or heteroalkyl; or both of W together can represent one single bond;

in Formula VII:

30 the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;

in Formula VIII:

the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10- positions;

in Formula IX:

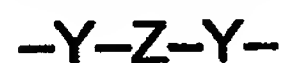
35 a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8 position; and



in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

10. An electronic device according to Claim 7, wherein the second  
5 monomeric unit has a formula



wherein:

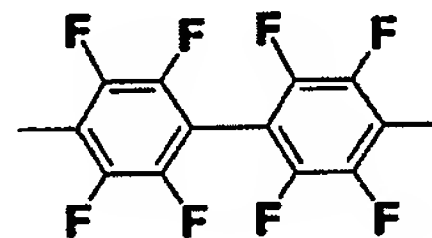
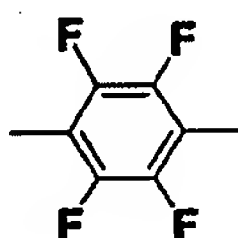
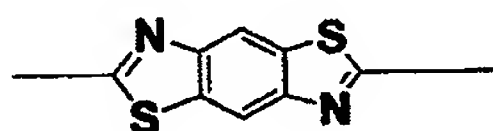
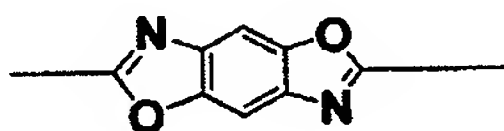
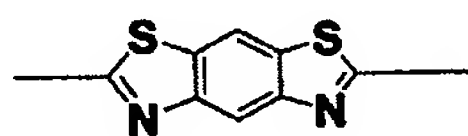
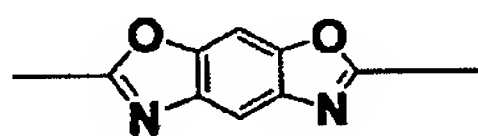
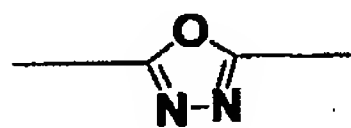
Y is an aromatic group with at least one substituent selected  
from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and  $NR^5$ ,  
10  $R^5$  is H or an alkyl; and  
Z is an electron deficient group.

11. An electronic device according to Claim 10, wherein Y is  
selected from fluorenes, spirofluorenes, phenyls, biphenyls, bridged  
biphenyls, naphthalenes, anthracenes, and combinations thereof.

15 12. An electronic device according to Claim 10, wherein Z is  
selected from oxazole-type groups, oxadiazole-type groups, thiazole-type  
groups, fluorinated aromatic groups, and combinations thereof.

13. An electronic device according to Claim 10, wherein Z is  
selected from:

20



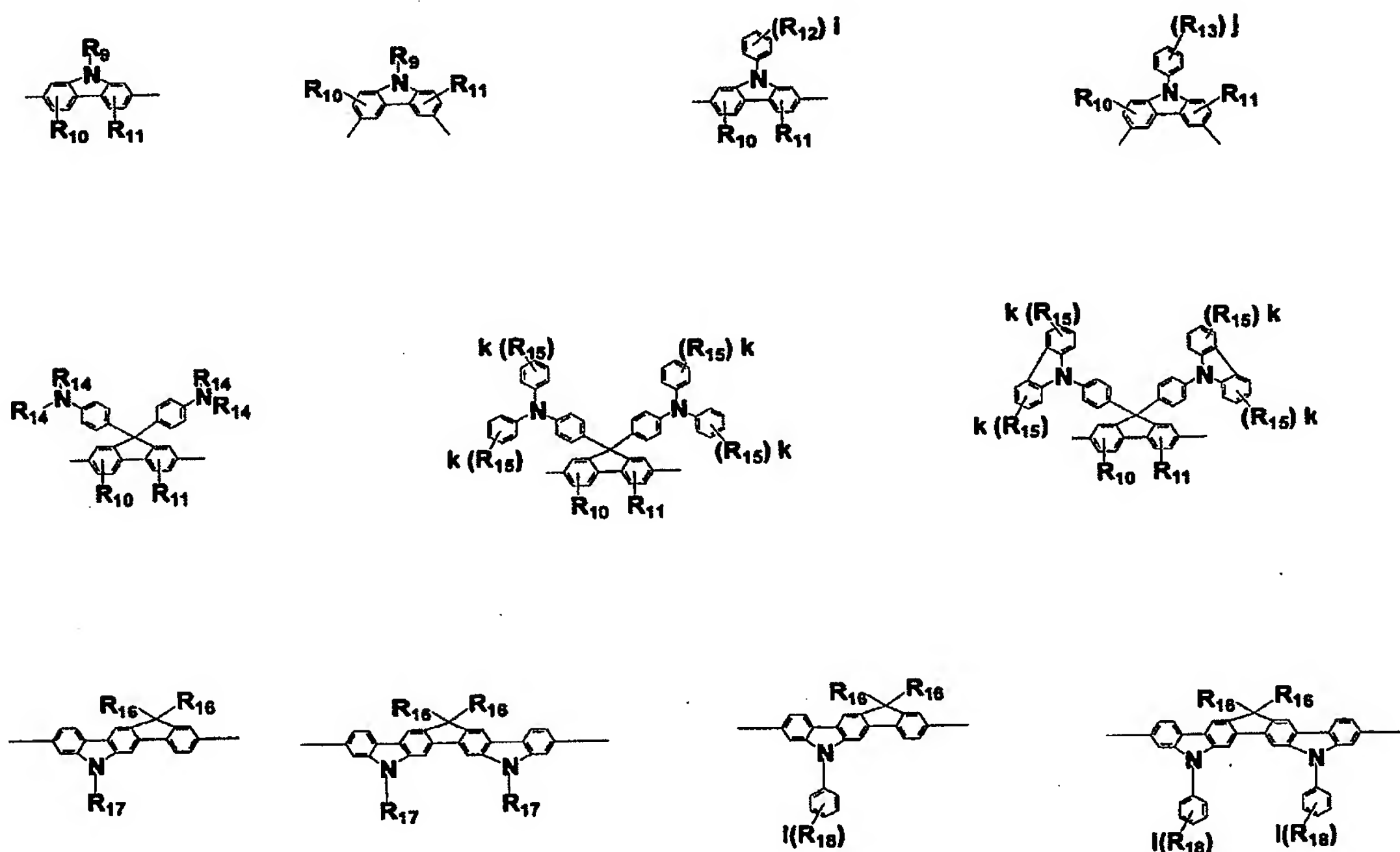
14. An electronic device according to Claim 7, wherein the second  
monomeric unit has hole transport properties.

25 15. An electronic device according to Claim 14, wherein the second  
monomeric unit is selected from carbazoles, triaryl amines, aromatic

groups having carbazole groups, aromatic groups having triarylamine groups, and combinations thereof.

16. An electronic device according to Claim 14, wherein the second monomeric unit is selected from:

5



wherein:

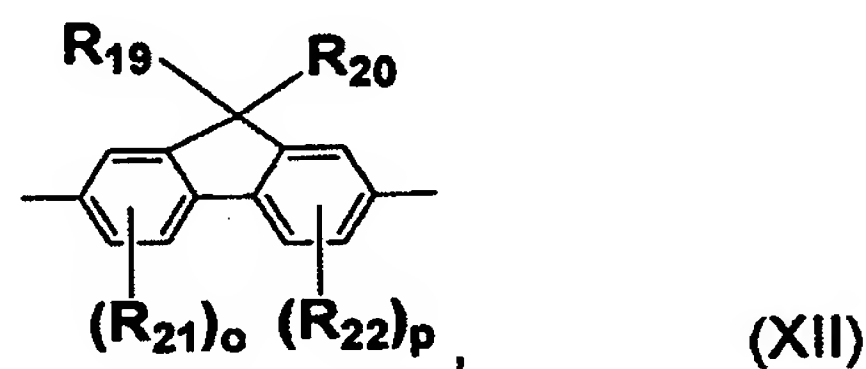
R9-R18 are same or different and are selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and  $NR^5$ ,  $R^5$  is H or an alkyl;

i, j, k, l are numbers of substituents on the benzene rings and are same or different and each of i, j, k, and l is in a range of 0-3.

17. An electronic device according to Claim 7, wherein the second monomeric unit is selected from substituted fluorenes, substituted phenyls, substituted biphenyls, substituted bridged biphenyls, and combinations thereof.

18. An electronic device according to Claim 7, wherein the second monomeric unit has Formula XII:

20



wherein

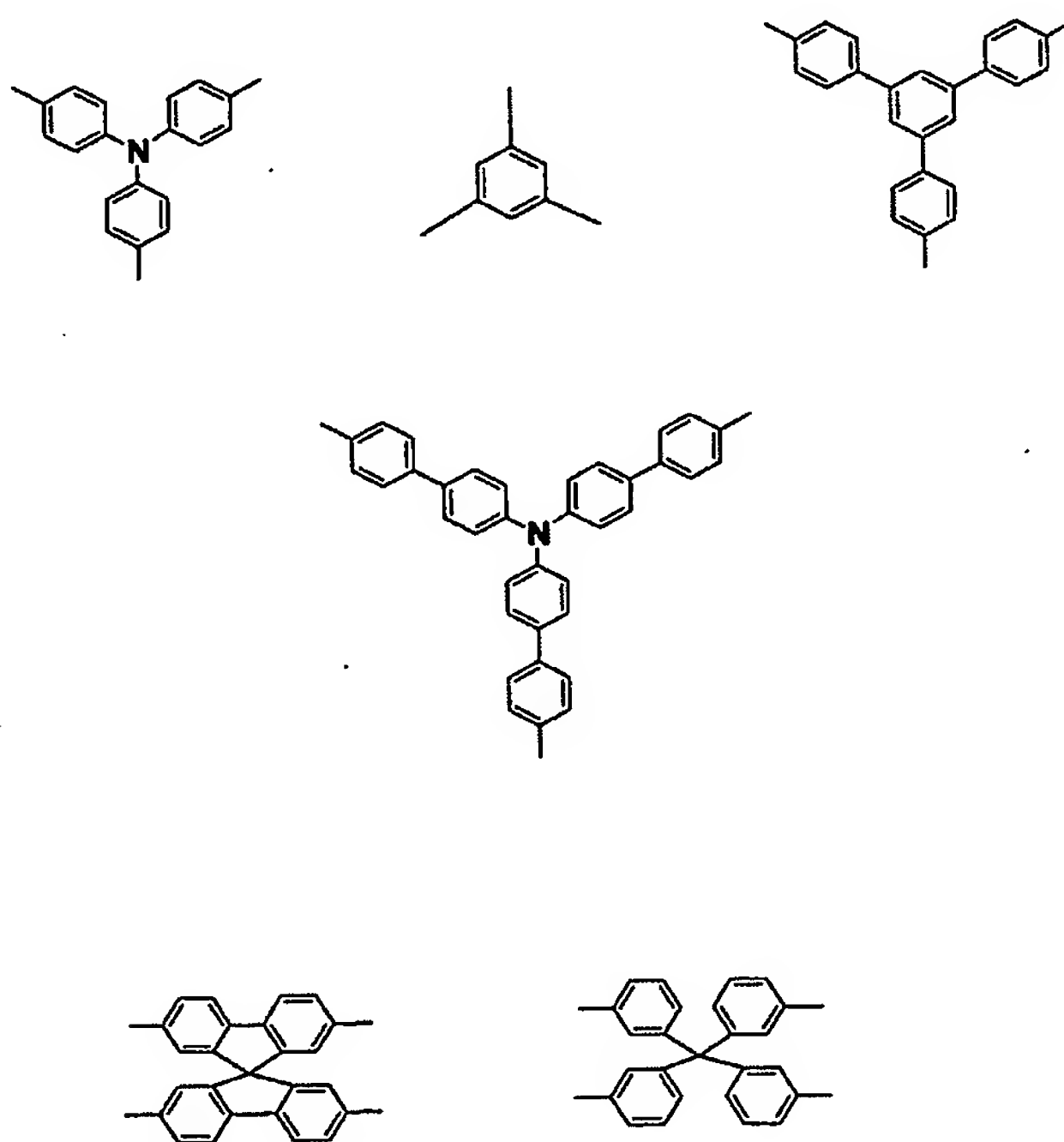
R19-R22 are same or different and are selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and N R<sup>5</sup>,

5 R<sup>5</sup> is H or an alkyl; and

o and p are numbers of substituents on the benzene rings and are same or different and each of o and p is in a range of 0-3.

10 19. An electronic device according to Claim 7, wherein the second monomeric unit is a branching monomeric unit having more than two linkage sites.

20. An electronic device according to Claim 19, wherein the second monomeric unit is selected from to:



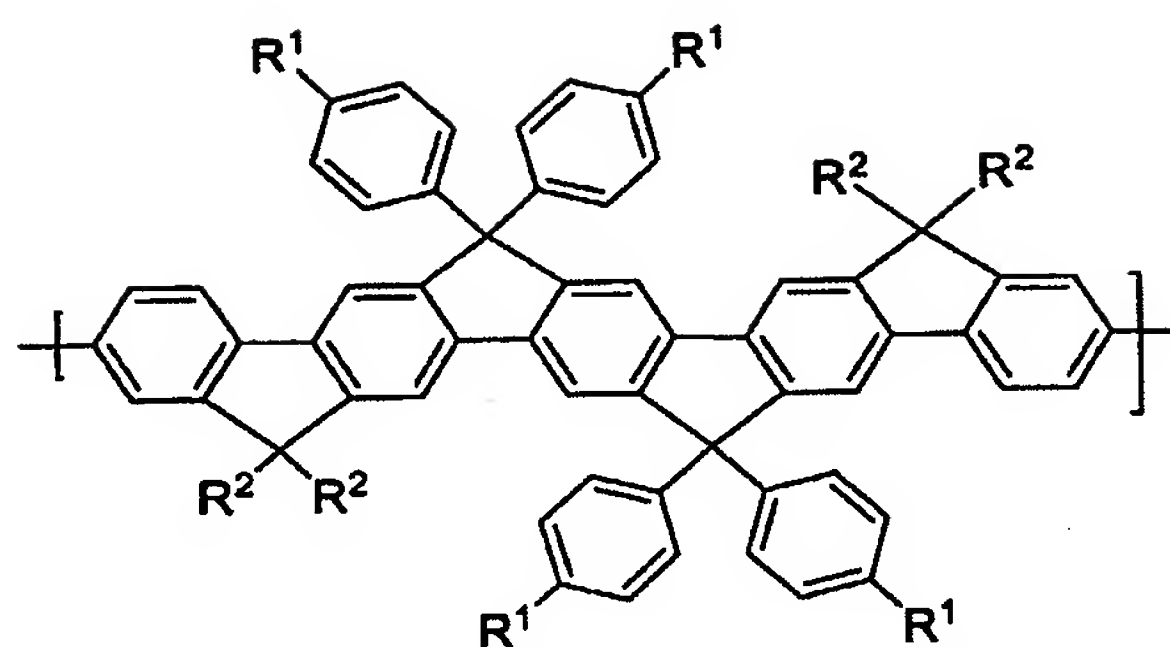
15

20. An electronic device comprising an active layer positioned between two electrical contact layers, wherein the active layer comprises a copolymer having the formula:

20 —(first monomeric unit)<sub>q</sub>—(ED unit)<sub>r</sub>—(SE unit)<sub>s</sub>—(HT unit)<sub>t</sub>—(branching unit)<sub>u</sub>—

wherein:

the first monomeric unit has Formula I:



(I)

wherein:

$R^1$  is the same or different at each occurrence and is selected from hydrogen,  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

$R^2$  is the same or different at each occurrence and is selected from  $C_1$ - $C_{20}$  alkyl,  $C_2$ - $C_{20}$  alkenyl,  $C_2$ - $C_{20}$  alkynyl,  $C_1$ - $C_{20}$  alkoxy,  $C_1$ - $C_{20}$  oxyalkyl,  $C_2$ - $C_{20}$  oxyalkenyl,  $C_2$ - $C_{20}$  oxyalkynyl,  $C_1$ - $C_{20}$  fluorinated alkyl,  $C_2$ - $C_{20}$  fluorinated alkenyl,  $C_1$ - $C_{20}$  fluorinated oxyalkyl,  $C_2$ - $C_{20}$  fluorinated oxyalkenyl,  $C_2$ - $C_{20}$  fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR<sup>3</sup>, -CO<sub>2</sub>R<sup>3</sup>, -SR<sup>3</sup>, -N(R<sup>3</sup>)<sub>2</sub>, -P(R<sup>3</sup>)<sub>2</sub>, -SOR<sup>3</sup>, -SO<sub>2</sub>R<sup>3</sup>, and -NO<sub>2</sub>; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

$R^3$  is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

the ED unit has a formula -Y-Z-Y- wherein:

Y is an aromatic group with at least one substituent selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR<sup>5</sup>,

$R^5$  is H or an alkyl; and

Z is an electron deficient group;

the HT unit is a monomeric unit having hole transport properties;

the SE unit is selected from substituted fluorenes, substituted phenyls, substituted biphenyls, substituted bridged biphenyls, and combinations thereof;

the branching unit is a monomeric unit having more than two  
5 linkage sites;

q is an integer; and

r, s, t, and u are 0 or an integer, with the proviso that at least one of r, s, t, and u is an integer.

10

1/1

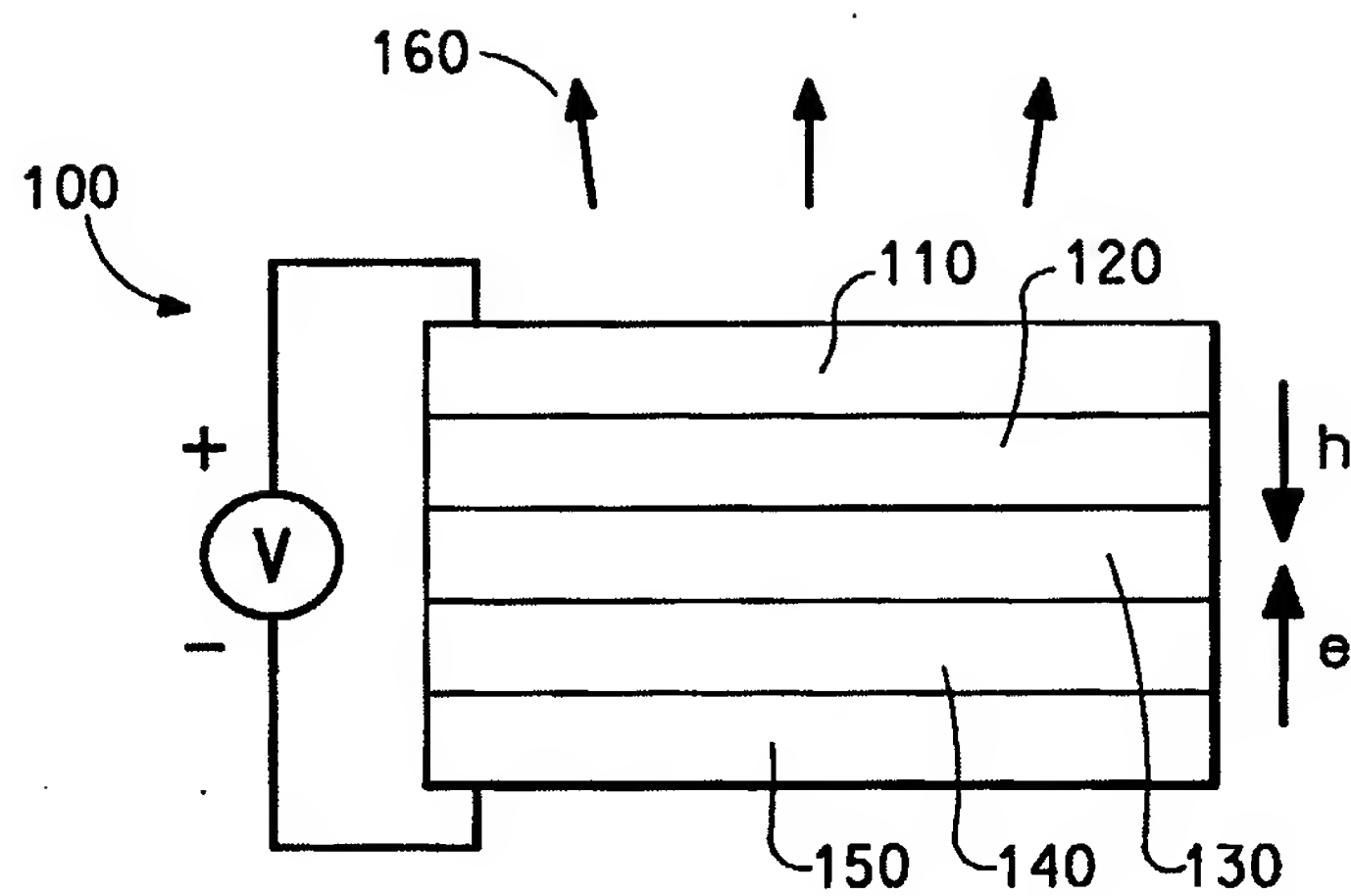


FIG. 1